

Polymer

ENGINEERING AND SCIENCE

POLYMER TOPICS

Polyblends—'84
National Research Council of Canada
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ENGINEERING AND SCIENCE

Published by the Society of Plastics Engineers

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Polymer Engineering and Science (ISSN 0032-3888) is printed at Waverly Press, Easton, MD 21601. Address changes, undeliverable copies and orders for subscriptions should be sent to Circulation Manager, Society of Plastics Engineers, 14 Fairfield Dr., Brookfield Center, Conn. 06805. Published monthly except for February, April, June, August, October, and December when published semi-monthly. Second-class postage paid at Brookfield Center, Conn., and additional entry offices. Accepted at special postal rate provided in P.M. Sec. 132.122.

Neither the Society of Plastics Engineers, Inc., nor *Polymer Engineering and Science* is responsible for the views expressed by individual contributors either in articles published in *Polymer Engineering and Science* or in technical papers presented at meetings of the Society.

Subscription rates for 1984. SPE members, 1 year—\$70, 2 years—\$125, 3 years—\$175. Nonmembers (U.S. and North America), 1 year—\$95, 2 years—\$170, 3 years—\$225. Corporate, institutional or library, 1 year—\$250. Postage charge for all subscriptions outside North America—\$18 per year. Air delivery outside North America—\$50 per year.



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Business and Executive Offices, 14 Fairfield Dr., Brookfield Center, Conn. 06805

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POLYMER ENGINEERING & SCIENCE is indexed by:—Chemical Abstracts—Engineering Index, Inc.

PREAMBLE

Polymer alloys and blends, PAB, constitute about 15 percent of all consumed plastics. Their consumption is increasing at a rate twice as high as that for all plastics (for engineering polymer alloys it is thrice as high). In 1983 the US sales of PAB reached the five-billion dollar mark. Especially during the last three to four years, PAB enjoyed ever increasing recognition, indicated by an exponential growth of the number of patents and technical publications.

Advantages of alloying are not only for engineering plastics, but also for commodity resin, frequently sold as a homologous polymer blend of superior processability and properties. Modification of impact strength (especially at low temperatures), dimensional stability, creep, and stress-cracking have been the prime goals of blending. Due to advances in alloying know-how the recycling industry is also growing. However, PAB technology still awaits a breakthrough in the methods of processing of immiscible blends to obtain a product retaining its desired properties. It is the link: processing-stable properties which will dictate the future of PAB. The current methods of stabilization by addition of a large (5 to 10 weight percent) amount of expensive compatibilizers (e.g. block polymers) needs to be critically examined.

Metal alloys have been with us for at least 6000 years. Since antiquity, developed by artisans and craftsmen, these materials were introduced to fulfill specific needs. It is difficult to imagine what history would be without them. The secrets of the ancient alloys are now being discovered. With the help of 20th-century solid-state physics we have begun to understand why they did work for millenia. With modern metallurgy, past industrial achievements are now being interpreted from the point of view of materials science. Progress in the area of modern metallic alloys is very impressive.

A similar time sequence for PAB is inconceivable. However, again there is a growing gap between what industry can do and what the material science can explain and predict. Starting with the phase equilibrium and ending with the fracture mechanics we see painfully clear evidence of the inadequacy of our understanding of materials behavior. It is true that the industrial polymer blends are complex

due to composition and process-influenced morphology, especially when the notorious non-equilibrium state of PAB is considered.

To facilitate the progress in PAB it is important to create and maintain a constant dialogue between the industrial engineers and material scientists. This is why the Industrial Materials Research Institute of the National Research Council of Canada (NRCC/IMRI) organizes and sponsors the annual symposia on PAB. The current issue of *POLYMER ENGINEERING AND SCIENCE* contains the proceedings of "Polyblends-'84", the fifth thematic meeting of this series. The four previous ones have been published in the same journal; viz. 22(2)(1982); 22(17)(1982); 24(2)(1984). To enhance the industry-academia interactions the number of participants at these symposia is kept small, with about an equal number of persons from the two groups. Due to the generous help of the editor of this journal we have been able to reach a much larger circle of interested people. Furthermore, the proceedings of all our symposia are recorded (presentations and discussions). The magnetic tapes are kept in the NRCC-IMRI library for a period of two years, available to anyone interested in the subject. This year for the first time a panel discussion was introduced to provide a forum for people from the plastics industry to express opinions and ideas on the present and future of PAB. At "Polyblends-'84" ten papers were presented in the customary sequence: thermodynamics (Jain and Simha, and Prud'homme and Riedl), compatibilization (Pillon and Utracki, and Eisenberg and Hara), rheology and mechanical properties (Rudin and Brathwaite, and Dumoulin, Farha, and Utracki), morphology and permeability (White and Min, and Kamal, Jinnah, and Utracki), processability (Baker and Catani) and recycling (Leidner-withdrawn from publication by the author). The papers reflect the growing concern in the scientific community for development of predictive methods of thermodynamical description of the blend behavior and influence of the polymer-polymer interaction on the flow/processability and on the properties of the finished product.

L. A. Utracki, Guest Editor,
Symposium organizer and Chairman

Statistical Thermodynamics of Blends: Equation of State and Phase Relations

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We discuss the free-energy expressions for homogeneous melts and their blends, based on our hole theory. Equation of state (PVT) and free energy of mixing (ΔG_m) are considered from a common point of view without the introduction of additional parameters to pass from the first to the second set of properties. Practical problems arise from the fact that ΔG_m represents a difference between large quantities. As illustrations we analyze two typical systems. One is the $n - C_6 + n - C_{16}$ pair where PVT and ΔG_m , the latter at atmospheric pressure only, have been studied experimentally. The other is $n - C_6$ with a low and high molecular weight respectively of polyethylene as solute. Here the PVT relations of the components only are known. The effects of intercomponent attractions, temperature, pressure, and molecular weight on phase behavior are investigated. Critical coordinates, lower critical-solution temperatures (LCST) and their pressure dependence are computed. An iso-free volume condition obtains for this dependence where free volume is defined by the hole fraction inherent in the theory. Comparisons with experimental observations and other theoretical computations for different molecular weights are limited by the effect of polydispersity. Moreover, cloud point curves are shown. We finally compute the composition and pressure dependence of the χ -parameter which is implicit in the theory. We conclude with some comments regarding polymer blends.

INTRODUCTION

Phase equilibria in multicomponent systems of low, high, and mixed molecular weights have been objects of extensive experimental and theoretical study. An important development was initiated by the Brussels school of Prigogine (1). They recognized that in addition to the combinatorial contribution to the entropy of mixing, equation of state contributions to the free energy of mixing must be taken into consideration. That is, such quantities as the internal pressure and the thermal expansivity of the components and their variations with changing molecular environment must be included. For a review of these ideas and their quantitative consequences see an Institute Symposium on the Thermodynamics of Liquids and Polymer Blends (2, 3). A successful theory of the equation of state thus should also provide the necessary input for an adequate prediction of the free energy of mixing and its compositional derivatives, with a minimum appeal to additional experimental information. The situation in the frame of Prigogine's

and of Flory's equation of state, and by means of corresponding states considerations has been extensively discussed (2, 4).

We have been concerned over the past years with the configurational statistical thermodynamics of chain molecular fluids. The essence of the theory is a cell model with additional disorder provided by lattice vacancies or holes. The physical basis and quantitative consequences have been reviewed at the symposium mentioned above (5). The equation of state is quantitatively successful in the domain of high molecular weights as well as of oligomeric systems, and for low and elevated pressures. Subsequently, the theory was generalized to multicomponent fluids (6). Most recently we have started to extend the theory to the free energy of mixing and to the ensuing phase equilibria (7). In other words, whereas previous work dealt with the volume derivatives of the free energy, we have now begun to investigate the compositional derivatives. In this paper we consider the equation of state of binary systems and then turn to the chemical potentials and lower critical-solution temperatures (LCST).

Low molecular weights are of interest per se, but also are instructive for the theory of polymer blends. Detailed experimental information exists for hydrocarbon mixtures and provides insight into the performance of the theory. Hence both types will be examined as binary blends.

THEORY

We start with the molar free energy F_i of component i , $i = 1, 2$, which equals (8):

$$\begin{aligned} F_i/RT = & \ln(y/s_i) + s_i y^{-1}(1-y)\ln(1-y) \\ & - (s_i - 1)\ln[(z-1)/e] \\ & - c_i \{ \ln[(M_{oi} V_i^*/N_A) Q^{-1}(1-\eta)^3] \\ & \cdot (2\pi M_{oi} kT/N_A h^2)^{3/2}] \\ & - (y/2\tilde{T}) Q^2 (A_1 Q^2 - 2A_2) \} \end{aligned} \quad (1)$$

with $Q = (y\tilde{V})^{-1}$; $\eta = 2^{-1/6} \cdot y Q^{1/3}$; $A_1 = 1.011$; $A_2 = 1.2045$. Here M_{oi} is the molecular weight of a segment, $v_i^* = V_i^* M_{oi}/N_A$ its repulsive volume, with V_i^* the corresponding specific volume, and $h = 1 - y$ the fraction of vacant sites in the quasi-lattice spanning the fluid. The tildes indicate reduced variables and the scaling parameters are derived by superposition of the experimental and reduced theoretical equation of state. We note that the free energy in Eq 1 contains two additive contributions. One of these is a function of volume and temperature, either explicitly or through y , see Eq 3 below, the remainder being independent of these variables. The first contribution to the total configurational free energy is pertinent for the pressure equation given by $P = -(\partial F/\partial V)_T$.

The resulting equation of state is:

$$\tilde{P}\tilde{V}/\tilde{T} = (1-\eta)^{-1} + (2y/\tilde{T})Q^2(A_1 Q^2 - A_2) \quad (2)$$

where the free-volume fraction $h = 1 - y$ satisfies the minimum condition on the free energy, viz.:

$$\begin{aligned} (s/3c)[(s-1)/s + y^{-1}\ln(1-y)] = & (\eta - 1/3) \\ \cdot (1-\eta)^{-1} + (y/6\tilde{T})Q^2(2A_2 - 3A_1 Q^2) \end{aligned} \quad (3)$$

Here $3c$ represents the number of effectively volume-dependent or external degrees of freedom in a chain consisting of s segments. The product $s_i M_{oi}$ equals the molecular weight nM_{rep} of the n -mer with repeat-unit molecular mass M_{rep} . The scaling parameters appearing in Eqs 2 and 3 for the components are defined as follows:

$$P_i^* = q_i z \epsilon_i^* / s_i v_i^*; \quad T_i^* = q_i z \epsilon^* / c_i k \quad (4)$$

with $q_i z = s_i(z-2) + 2$ the number of intermolecular contacts in the lattice with coordination number z and ϵ_i^* the maximum segmental-pair attraction energy. These definitions establish the following important relation for each of the components:

$$P^* V^* / T^* = (c/s) R / M_o \quad (5)$$

The generalization to multicomponent systems leaves Eqs 2 to 4 formally unaltered (6), provided the parameters are redefined as functions of composition. That is, s and c become number averages,

and M_o a weight average. Moreover, averages of the three scaling parameters in Eq 4 now involve mean values $\langle \epsilon^* \rangle$ and $\langle v^* \rangle$ satisfying the following relations:

$$\begin{aligned} \langle \epsilon^* \rangle \langle v^* \rangle^2 = & X_1^2 \epsilon_{11}^* v_{11}^{*2} \\ & + 2X_1 X_2 \epsilon_{12}^* v_{12}^{*2} + X_2^2 \epsilon_{22}^* v_{22}^{*2} \quad (6) \\ \langle \epsilon^* \rangle \langle v^* \rangle^4 = & X_1^2 \epsilon_{11}^* v_{11}^{*4} \\ & + 2X_1 X_2 \epsilon_{12}^* v_{12}^{*4} + X_2^2 \epsilon_{22}^* v_{22}^{*4} \end{aligned}$$

The X_i are the site fractions corresponding to the mole fractions x_i , or $X_i = x_i q_i / \sum x_i q_i$. These are the weighting factors in Eq 6 for the "self" interactions 1-1 and 2-2 and cross interaction 1-2 parameters. An important consequence regarding Eq 5, as applied to the mixture, follows from the foregoing. The right hand side is completely defined by the properties of the components. For the components the value $3c_i/(s_i + 3) = 1$ has been adopted previously (5, 6). It follows that the identical value obtains for the ratio $3\langle c \rangle / (\langle s \rangle + 3)$. If now the averages $\langle V^* \rangle$ and $\langle T^* \rangle$ for a given composition are obtained from the atmospheric pressure isobar ($\tilde{P} \approx 0$), $\langle P^* \rangle$ is computable and serves to predict the volume at elevated pressures without further recourse to experiment.

The molar free energy F_m of the binary system equals (6):

$$\begin{aligned} F_m/RT = & x_1 \ln x_1 + x_2 \ln x_2 \\ & - (\langle s \rangle - 1)\ln[(z-1)/e] \\ & + \ln(y/\langle s \rangle) \\ & + \langle s \rangle y^{-1}(1-y)\ln(1-y) \quad (1a) \\ & - \langle c \rangle \{ \ln[(M_o V^*)/N_A] Q^{-1} \\ & \cdot (1-\eta)^3 (2\pi \langle M_o \rangle kT/N_A h^2)^{3/2}] \\ & - (y/2\tilde{T}) Q^2 (A_1 Q^2 - 2A_2) \} \end{aligned}$$

Equation 1a displays a complex dependence on composition through the scaling parameters and the free-volume function. The function of interest is the difference $\Delta G_m = G_m - x_1 G_1 - x_2 G_2$, with $G = F + PV$. The changes $\Delta \mu_i$ of the chemical potentials are obtained from the relationships:

$$\begin{aligned} \Delta \mu_1 = & \Delta G_m - x_2 (\partial \Delta G_m / \partial x_2)_{P,T} \\ \Delta \mu_2 = & \Delta G_m + x_1 (\partial \Delta G_m / \partial x_2)_{P,T} \end{aligned} \quad (7)$$

In the practical applications of Eq 7, we compute ΔG_m for a specified T and P as a function of composition and then approximate the theoretical function by least square polynomials of appropriate degree (see below).

EQUATION OF STATE OF BLENDS

Consider the pair n-Hexane + n-Hexadecane. Isotherms and isobars of components and mixtures over a range of 75 degrees and up to ~5 kbar have been presented by Dymond, *et al.* (9) and discussed in terms of theory by us (6). Figure 1 shows the experimental and theoretical isobar at atmospheric

pressure, including the components. The straight line relationships seen are the approximations to the solutions of the coupled Eqs 2 and 3. Figure 2 displays a series of isotherms at two temperatures. To the experimental (circles) and computed (lines) volumes have been added the results of the empirical Tait equation (triangles), which is of no further concern here. Recall again that the lines for the blends are computed without further experimental input, once the intercepts are determined. The maximum deviation, 0.8 percent in V , is encountered for $n - C_6$ at the highest temperature.

The compatible poly(2,6-dimethyl-1,4-phenylene ether)-polystyrene blend has been studied experimentally by Zoller and Hoehn (10), and the results have been evaluated (11). The comparison between theory and experiment again shows good agreement for the equation of state.

FREE-ENERGY RELATIONS

The free energy of mixing and ensuing chemical potentials for the $n - C_6$, $n - C_{16}$ pair have been obtained by means of activity measurements (12). The data are summarized by the authors in terms of accurate polynomials for the excess quantities.

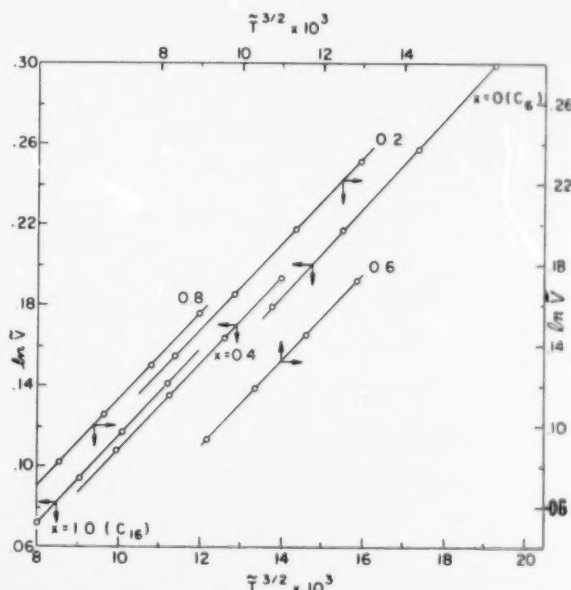


Fig. 1. Isobars of $n - C_6$, $n - C_{16}$, and their mixtures at atmospheric pressure: lines, theory; circles, experiment.

Single-phase conditions obtain. Equations 1, 1a, 2 and 3 yield the results for ΔG_m seen in column 5 of Table 1, employing the parameters displayed in columns 2 to 4. Significant disagreement with experiment (column 6) is noted. Now the energy quantities are scaled by the products $\langle P^* \rangle \langle V^* \rangle$ and $P^* V^*$, respectively. The $\langle P^* \rangle$ in column 4 are predicted from the analog of Eq 5. Thus one may question the accuracy, although not the basic correctness of this equation. Particularly so, since the quantity ΔG_m represents a difference of numerically large terms. Hence it is reasonable to inquire what revisions in $\langle P^* \rangle$ -values are required to obtain adequate values of ΔG_m , assuming that all other parameters for the blend and all corresponding quantities for the components are adequate. The adjustments, see column 7, are so minor that they leave the theoretical equation of state unaltered. Actually, and as one should expect, the P_i^* as extracted from pressure data are subject to small

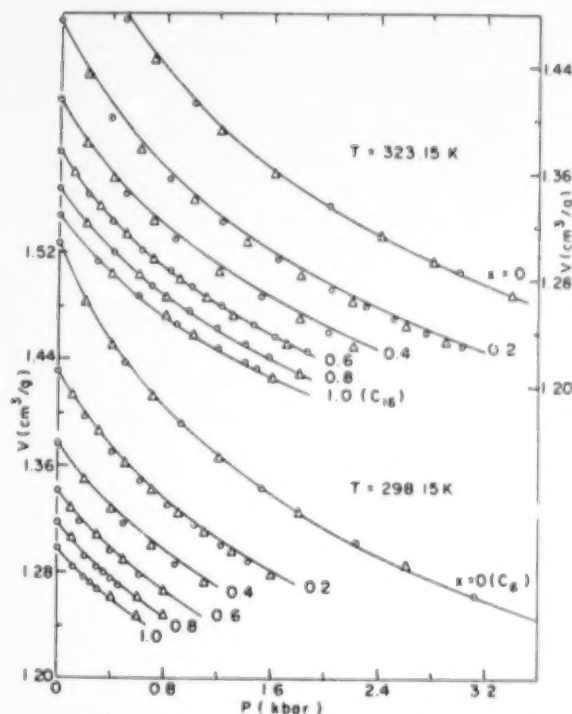


Fig. 2. Isotherms of $n - C_6$, $n - C_{16}$, and their mixtures: lines, theory, Eqs. 2 and 3; circles, experiment; triangles, Tait equation.

Table 1. Scaling Parameters, Free Energy ΔG_m , and Chemical Potential $\Delta \mu_1: x_1 n - C_6 + x_2 n - C_{16}$.
 $T = 293.15 \text{ K}$

x_1	$\langle V^* \rangle^a, \text{cm}^3/\text{g}$	$\langle T^* \rangle^a, \text{K}$	$\langle P^* \rangle^a, \text{bar}$	$-\Delta G_m/RT$		$\langle P^* \rangle^c (\text{Adj.}) \text{bar}$	$-\Delta G_m/RT (\text{Adj.})$		$-\Delta \mu_1/RT$	
				Theory	Exp. ^b		Theory ^c	Quadratic	Theory ^c	Exp. ^b
0	1.2090	7448	6785							
0.2	1.2134	7131	6813	0.399	0.518	6825	0.515	0.516	1.62	1.68
0.4	1.2222	6799	6878	0.707	0.699	6878	0.707	0.700	0.98	0.95
0.5	1.2289 ^d	6626 ^d	6930 ^d	0.881	0.720	6909	0.719	0.723	0.73	0.72
0.6	1.2362	6433	6993	0.997	0.698	6951	0.698	0.700	0.52	0.53
0.8	1.2509	5895	7088	0.706	0.517	7056	0.519	0.517	0.24	0.23
1.0	1.2763	5197	7201							

^a From Reference (6). ^b Reference (12). ^c See text. ^d Interpolated parameters.

fluctuations of the order of a few percent at most, which are then smoothed out. The differences between columns 4 and 7 are so small that literal agreement between recomputed and experimental ΔG_m 's would require more significant figures than can be justified. The analysis is completed by fitting a quadratic equation to ΔG_m , see column 9, and employing Eq 7 to compute $\Delta\mu_1$, column 10, with experimental values in the last column. The adjustment, once made, suffices to yield good agreement for a temperature increase of 40 degrees (7).

The example shown indicates that the theory describes both the equation of state and the configurational free energy of a blend. We have not investigated other low-molecular-weight pairs along analogous lines. However the results for the equation of state (6) suggest a similar situation as illustrated here. The procedures indicated then in practice consist of dilatometric measurements at atmospheric pressure which yield the scaling parameters $\langle V^* \rangle$ and $\langle T^* \rangle$. This provides a first value of $\langle P^* \rangle$ by means of Eq 5 on substitution of the appropriate averages. Free-energy or enthalpy measurements at atmospheric pressure then serve to extract an improved pressure parameter for the mixture, if required. This then makes predictions of volumes and excess energies at elevated pressures possible.

POLYMER SOLUTIONS

Here we proceed in a different manner (7). We will illustrate by means of a particular example the effects of the cross-interaction parameter ϵ_{12}^* , pressure, and molecular weight on phase equilibrium.

Consider polyethylene in n-hexane. The equation of state of both components has been analyzed. For the polymer two sets of measurements are available (13, 14), but we employ the scaling parameters derived in the former. Since we are unable to solve Eq 6 for $\langle \epsilon^* \rangle$, $\langle v^* \rangle$ without a knowledge of ϵ_{12}^* and v_{12}^* , we simply take the average $[(V_{11m}^{1/3} + V_{22m}^{1/3})/2]^3 = 40.0 \text{ cm}^3 \text{ mol}^{-1}$. For $n = C_6 + nC_{16}$ this equation yields a value close to the average of the weakly varying V_{12}^* (see Table 4 of Ref. 6). The characteristic ratio $\epsilon_{12}^*/\epsilon_{11}^*$, where index 1 here refers to hexane, in the same table varies between 1.03 and 1.00. We examine here two values, namely 1.00 and 1.02. Finally we assume for our calculations ideally homodisperse polymer samples. Three molecular weights will be used, namely $M = 8000$; 28,000; and 177,000. The latter two correspond to the averages in experimental studies (15, 16). The corresponding segmental chainlengths for the polymer (6) are $s_2 = 252.2$, 882.7, and 5580.1. For C_6 we have $s_1 = 2.5$. Equation 6 then yields $\langle \epsilon^* \rangle$ and $\langle v^* \rangle$.

With the information at hand, Eqs 1 to 3 and 6 yield the free-energy change ΔG_m . The variation with composition is larger than for the low-molecular-weight blend. Moreover we wish to investigate conditions for phase separation. Hence the theoretical free-energy changes were approximated by quartics in the mole fraction of polymer, i.e.:

$$\Delta G_m/RT = \sum_0^4 a_i x^i \quad (8)$$

The chemical potentials and their derivatives then follow from Eq 7. Analogous results were computed for pressures of 50 and 100 bar. Figure 3 displays the chemical potentials for the three pressures with $\epsilon_{12}^* = \epsilon_{11}^*$, and a molecular weight of 8000. Figure 4 depicts the analogous results with $\epsilon_{12}^* = 1.02\epsilon_{11}^*$. The critical polymer concentration x_c and the critical temperature T_c are indicated in the figures. They were derived by applying to Eq 8 the conditions of vanishing first and second compositional derivatives of $\Delta\mu_1$. This requires the validity of the following set of identities between the coefficients a_i :

$$\begin{aligned} x_c &= -a_3(4a_4)^{-1} = -(2/3)a_2a_3^{-1} \\ &= [a_2(6a_4)^{-1}]^{1/2} \quad \text{and} \quad a_3^2 = (2/3)a_2a_4 \end{aligned} \quad (9)$$

We observe a significant increase of the LCST with an even slight increase of the attraction energy between the two components, and a similar effect with increasing pressure. However, the critical compositions are hardly affected.

A qualitative understanding of the above trends is provided by the behavior of the free-volume quantities. As has been discussed repeatedly (2, 3), the differences between the two components in this respect are important in generating a LCST. With increasing temperature, these differences between high and low molecular weight are enhanced. Similarly, an increase in pressure reduces the disparity and hence necessitates a compensating increase in

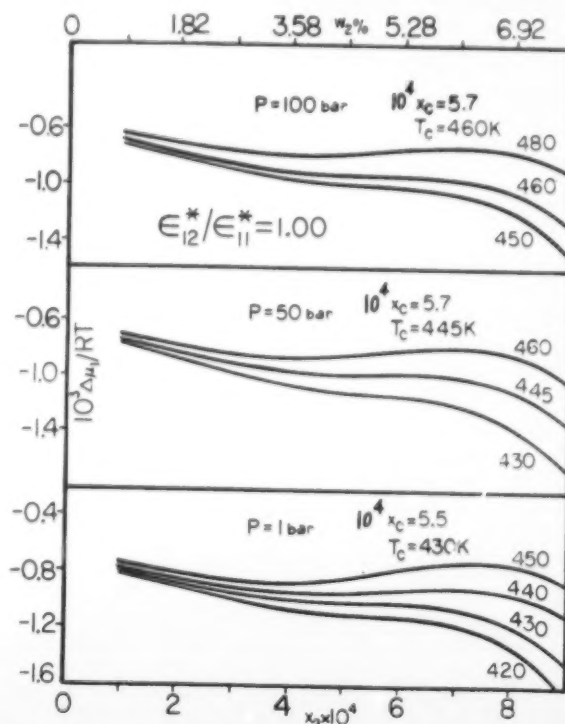


Fig. 3. Excess chemical potential of $n - C_6$ in polyethylene ($M = 8 \times 10^3$) as a function of polymer concentration in the critical temperature range for three pressures; $\epsilon_{12}^* = \epsilon_{11}^*$.

temperature to produce phase separation. Our quantitative evaluation of a characteristic free-volume fraction as a function of volume or pressure and temperature suggests an exploration of possible correlations between free-volume function and T_c . In Fig. 5 the difference $h_1 - h_2 = y_2 - y_1$ between

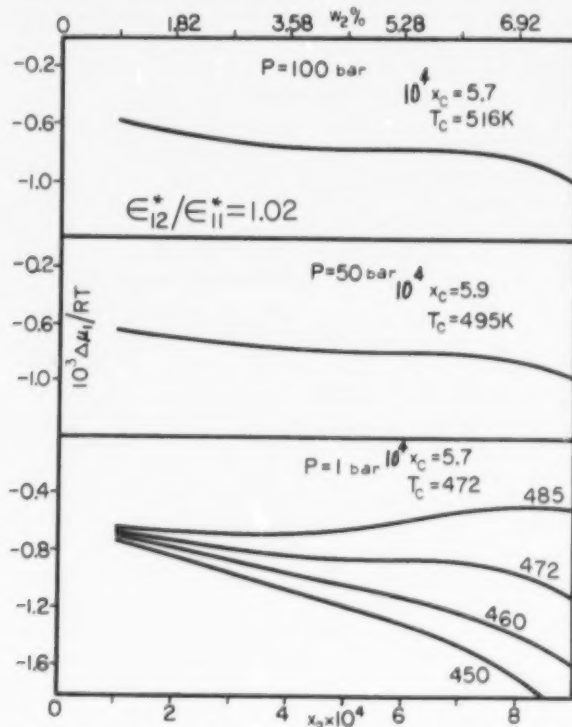


Fig. 4. Excess chemical potential $\epsilon f n - C_0$ in polyethylene ($M = 8 \times 10^3$) as a function of polymer concentration in the critical temperature range for three pressures; $\epsilon_{12}^*/\epsilon_{11}^* = 1.02\epsilon_{11}^*$.

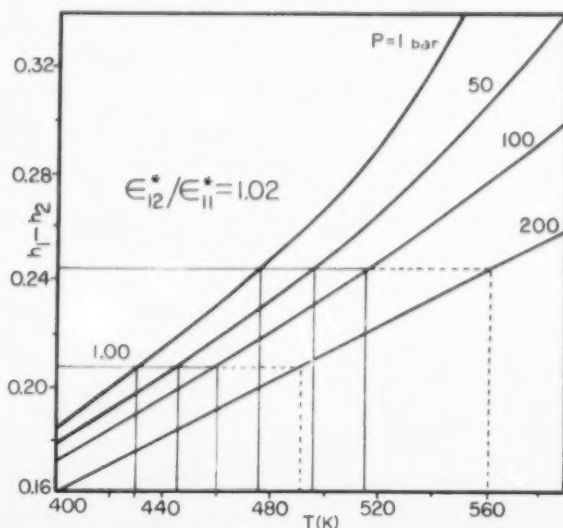


Fig. 5. Fractional free-volume difference $h_1 - h_2$, $n - C_0$ and polyethylene ($M = 8 \times 10^3$) as a function of temperature for $P = 1, 50, 100$, and 200 bar. Location of T_c for each isobar is indicated by the guide lines. Dashed lines, extrapolated values for $P = 200$ bar and two values of $\epsilon_{12}^*/\epsilon_{11}^* = 1.00$, lower line and 1.02 , upper line.

the hole fractions of the two components is displayed as a function of temperature for a series of pressures, and the two values of the energy ratio. At fixed magnitude of this ratio, criticality is reached at a constant value of $h_1 - h_2$, namely ≈ 0.21 and 0.24 , respectively. Thus the pressure dependence of T_c is determined by an iso-free volume condition. A linear variation ensues with $dT_c/dP \approx 0.30$ and 0.42 K/bar, respectively. As an example, one can estimate a critical temperature of approximately 560 K for a pressure of 200 bar.

Next we compute cloud point curves (7). The condition $\Delta\mu_1 = \Delta\mu_2$ and Eq. 7 yield the results displayed in Fig. 6 for the three pressures. Graphical solutions were used, which could be improved. As seen, these curves can approximately be converted into a single master curve for the difference $T - T_c$.

Analogous calculations for $\epsilon_{12}^* = \epsilon_{11}^*$ are carried out next for molecular weights of $177,000$ and $28,000$. Compared with the previous case, both critical temperature and composition are displaced to lower values. At atmospheric pressure, $T_c = 395$ and 416 K, respectively, compared with the previous 430 K, and $x_c = 1.0 \times 10^{-5}$ and 1.7×10^{-5} or weight fractions of 0.020 and 0.054 , versus 5.5×10^{-4} and 0.049 for $M = 8000$.

The selection of the *n*-hexane + polyethylene pair was motivated by our previous analysis of the equation of state of the components and information from a low-molecular-weight analog (6). It is appropriate at this point to recall experimental (15 to 20) and theoretical (2, 16, 17, 21) results in the literature on similar pairs. Table 2 presents a summary

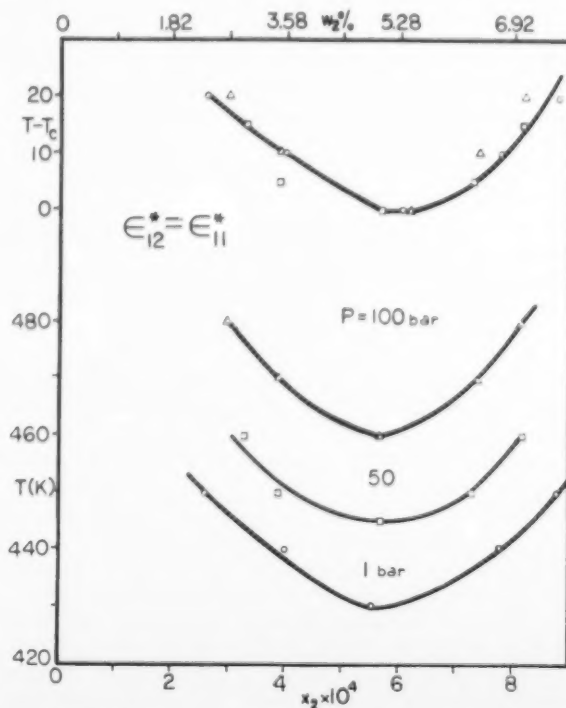


Fig. 6. Cloud point curves, for $P = 1, 50$, and 100 bars, $n - C_0$ and polyethylene ($M = 8 \times 10^3$) and a master curve.

Table 2. Critical Coordinates: n-Hexane + Polyethylene.

M_2	LCST, °C		dT_c/dP K/bar	$\Delta h, T = T_c$	$w_2\%, T = T_c$	
	Observed	Calculated			Observed	Calculated†
177,000	127°, 135°, 133°, 145°	70°, 91°, 122†	0.18	0.18	~2°, ~1°	2.0
28,000	150°	143†	0.25	0.20	—	5.4
8000	—	157†	0.30	0.21	—	4.9

† This work, $\epsilon_{12}^* = \epsilon_{11}^*$. * Ref. 20, $M_2 = 10^6$. ° Ref. 17, $M_2 = 1.8 \times 10^6$. ° Ref. 19, M_2 extrapolated to infinity. ° Ref. 16, $M_2 = 1.77 \times 10^6$. ° Ref. 21, ° Ref. 15, $M_2 = 28,000$.

of our computed critical coordinates and of *threshold* temperatures with corresponding compositions for the various polydisperse systems investigated. Quantitative discussions at this stage are prevented by the presence of polydispersity of, it appears, unknown magnitude. Our predictions are at least reasonable in the light of the body of observations. Moreover, pressure coefficients are similar to some observed (16, 21).

DISCUSSION

We conclude that a consistent description with a single set of parameters accounts for both volume and compositional derivatives, as is demonstrated for the $C_6 + C_{16}$ pair which we consider as a typical example. Concerning polymer components, we have so far not dealt with the influence of molecular-weight distribution. We see no simple average or ratios of moments emerging from our free-energy expressions. Spinodals and UCST's also have been left out.

A comment about the interaction parameter χ is in order. It plays a prominent role in other theories, albeit more so in a semi-empirical manner. Moreover, as is discussed in another presentation at this Symposium, it is amenable to determination by a variety of experimental methods. This quantity does not appear explicitly in the theory. However it is implicitly contained in our free energy expressions. We expect it to be a function of molecular weight, composition, pressure, and of course temperature, and the ratio $\epsilon_{12}^*/\epsilon_{11}^*$, as has been amply demonstrated in the literature. In our frame the χ -function is defined by the following expression in terms of the volume fractions ϕ_i :

$$x_1 \phi_2 \chi = \Delta G_m / RT - (x_1 \ln \phi_1 + x_2 \ln \phi_2) \quad (10)$$

with ΔG_m given by Eqs 1, 2, and their analogs for the mixture. We have evaluated Eq 10 for the polymer solution with $M_2 = 177,000$, $\epsilon_{12}^*/\epsilon_{11}^* = 1$, in the neighborhood of the critical temperature. A significant increase of χ with increasing ϕ_2 occurs which starts to level off in the critical concentration region with $\chi \approx 0.5$. An approximately linear relationship with $1/T$ obtains at a fixed composition near the critical point, in accord with observations in the literature. Finally with increasing pressure, χ (critical) increases slowly, about 2 percent for 100 bar. Again, it remains to investigate the lower molecular weight.

The position of the theory in respect to polymer blends, other than for the equation of state, remains to be established. How does the interplay between free volume and cross-interaction change with in-

creasing molecular weight? Can we approximately model the introduction of a few interactive centers for compatibilization by an ϵ_{12}^* without disturbing the contributions of the components? Ultimately of course, the whole theory will have to be generalized to copolymers.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation through Grants DMR 80-12232, and DMR 84-08341, Polymers Program. R. K. Jain is on leave from Rajdhani College, University of Delhi, New Delhi-110015, India.

REFERENCES

1. I. Prigogine, A. Bellemans, and V. Mathot, "The Molecular Theory of Solutions," North Holland Publishing Co., Amsterdam (1957).
2. D. Patterson, *Polym. Eng. Sci.*, **22**, 58 (1982).
3. T. Somcynsky, *ibid.*, **22**, 64 (1982).
4. O. Olabisi, L. M. Robeson, and M. T. Shaw, "Polymer-Polymer Miscibility," Academic Press, New York (1979).
5. R. Simha, *Polym. Eng. Sci.*, **22**, 74 (1982).
6. R. K. Jain and R. Simha, *Macromolecules*, **13**, 1501 (1980).
7. R. K. Jain and R. Simha, *Macromolecules*, **17** (1984).
8. R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).
9. J. H. Dymond, K. J. Young, and J. D. Isdale, *J. Chem. Thermodyn.*, **11**, 887 (1979).
10. P. Zoller and H. H. Hoehn, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1385 (1982).
11. R. K. Jain, R. Simha, and P. Zoller, *ibid.*, **20**, 1399 (1982).
12. M. L. McGlashan and A. G. Williamson, *Trans. Faraday Soc.*, **57**, 588 (1961).
13. O. Olabisi and R. Simha, *Macromolecules*, **8**, 211 (1975).
14. P. Zoller, *J. Polym. Sci. Polym. Phys. Ed.*, **16**, 1491 (1978).
15. A. Nakajima and F. Hamada, *Kolloid-Z.*, **205**, 55 (1965).
16. L. A. Kleintjens and R. Koningsveld, *Colloid Polym. Sci.*, **258**, 711 (1980).
17. R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **89**, 6822 (1967).
18. D. Patterson, G. Delmas, and T. Somcynsky, *Polymer*, **8**, 503 (1967).
19. F. Hamada, K. Fujisawa, and A. Nakajima, *Polym. J.*, **4**, 316 (1973).
20. P. I. Freeman and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).
21. A. T. Rodriguez and D. Patterson, *J. Chem. Soc., Faraday Trans.*, **78**, 501 (1982).

DISCUSSION

D. D. Patterson: With the equation of state you are emphasizing the role of free volume and energy in these mixtures. By implication this relates to polymer blends. Could you tell us if the introduction of free volume into the problem of polymer blends changes in any way the qualitative feeling that in order to get a miscible polymer system you must have special attractive centers, or so called specific interactions giving a negative value of this χ -parameter.

R. Simha: Free volume disparities in polymeric blends will be reduced and one will have to rely on particular interactive centers to accomplish compatibilization. We might speculate that at high pressures and with liquids of different compressibilities, one could generate sufficient disparity and require a weaker attraction to produce a negative excess enthalpy. However, at elevated pressures there is a limitation in respect to temperature, due to the opposing requirements of avoiding the onset of the glass transition and degradation.

L. A. Utracki: For practical reasons we do not use monodisperse polymers. My first question is: when will we be able to apply your theories to practical, polydisperse systems? This is a far from simple problem. Even the two component polymer-solvent system, as demonstrated experimentally by Ron Koningsveld, can produce a rather complex-looking, multipeak phase-equilibrium curve. Can this be predicted? Then let us go a step further, to the mixture of two polydisperse polymers. When can we hope to get the theoretical prediction of the binodal/spinodal for polymer blends? Let us take a simple case—say a mixture of linear with branched polymer such as polyethylene. Even this would be a very valuable guide for predicting the flow properties of polyethylene alloys.

R. Simha: You have touched upon questions which we hope to address in the frame of the theory sketched. Inspection of the free energy expressions indicates that no simple average chainlength or ratio of moments, as in the theory of Kleintjens and Koningsveld, applies. Thus the dependence of crit-

ical temperatures, binodals and spinodals on the molecular weight distribution remains to be explored. One can study experimentally such effects by comparing the results for nearly homodisperse polymers and their synthetic mixtures. In an analogous manner we should perform the corresponding computations. At present there are results for the LCST of single molecular weights only, as seen in Table 2. These will have to be compared with corresponding information for the blends of the same mean molecular weight.

L. A. Utracki: Judging by the experimental observations from Geleen, one may have a lot of trouble with polymers having a relatively narrow distribution of molecular weights; this is where Ron Koningsveld was getting rather complex looking spinodals. However, if the molecular weight is broad, one can expect to generate an overlapping series of curves smoothing out the phase separation diagram. In this particular case, it may be possible to define an appropriate average or averages of molecular weight and use these with the expressions derived for the monodisperse case. The question would be what type of molecular weight distribution one would have to have in order to be able to use this approximation.

R. Simha: The kind of model computations mentioned above should answer the points you raise. I also refer you to a recent comprehensive theoretical study of the influence of polydispersity and of the (assumed) concentration dependence of the χ -function by Šolc, Kleintjens, and Koningsveld, *Macromolecules*, 17, 573 (1984).

CORRECTION

There was an omission in the October 1984 POLYMER ENGINEERING AND SCIENCE paper by D. L. Faulkner entitled, "Anisotropic Aspects of the Environmental Stress Cracking of Acrylonitrile-Butadiene-Styrene and Styrene-Acrylonitrile Copolymers in Methanol." On page 1178, Figure 9 should carry the following caption: Annealed and unannealed plaques of Tyril (SAN).

The Determination of the Thermodynamic Interaction Parameter χ in Polymer Blends

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The miscibility of polymer blends is related to the polymer-polymer interaction parameter χ_{23} . Several methods can be used to evaluate this parameter and five of the most important ones are reviewed: two equilibrium methods (melting-point depression and vapor sorption), a transport method (inverse-phase gas chromatography) and two scattering methods (neutron scattering and small-angle x-ray scattering). Examples are cited where χ_{23} values for a given blend were determined by several of these methods. This comparison leads to the conclusion that a reasonable agreement is often reached despite conceptual differences between the methods involved.

INTRODUCTION

The use of polymer blends has gained increasing attention as an alternative to the development of novel polymers in the search for new materials and/or lower costs. Better characterization of blends in general is desirable but it could also be of benefit for polymer recycling schemes.

The miscibility of a polymer blend is controlled, like that of any other mixture, by thermodynamic factors, although kinetic considerations may still prevent phase separation of a thermodynamically unstable (metastable) blend. In the classical Flory-Huggins theory, and in the more recent "equation of state" theory, a thermodynamic interaction parameter χ is generally used as a measure of both the enthalpic and excess entropic interactions between the components of the blend (1 to 3). A negative value of this parameter indicates a local deviation from a random distribution of the number of contacts (or surface of contact) between molecules of like and unlike species. This deviation is caused by a chemical interaction between like and unlike molecules.

If polymers behaved like small molecules, polymer miscibility would imply solubility on a molecular scale. However, polymers do not necessarily follow such a simple behavior, and miscibility of polymer blends is determined not only by steric and chemical factors, also characteristic of small molecules at equilibrium, but also by the extent of interpenetration of polymer coils and the viscosity of the two polymers. As a matter of fact, the high viscosity of the medium may prevent reaching equilibrium and may lead to domain formation. For this reason, the use of thermodynamic data to rationalize or predict blend behavior may not be as general

as one would like it to be. However, other methods (mostly spectroscopic) also suffer from a similar limitation and the simplicity and universality of the thermodynamic approach is still a major advantage.

Several techniques can be used to determine χ . It is the main objective of this paper to review the most important ones and to compare results obtained by different methods on similar systems. Two equilibrium methods (melting-point depression and vapor sorption), one transport method (inverse-phase gas chromatography) and two scattering methods (neutron and small-angle x-ray scattering) were selected for that purpose.

THE χ PARAMETER

Originally, in the Flory-Huggins theory, χ_{12} was meant to represent the noncombinatorial free energy of interaction per solvent molecule, divided by RT , in a solvent-polymer system. Since polymer molecules vary in size, the use of a parameter defined in this manner may create problems. In a ternary system, made up of a small quantity of solvent (component 1, referred to as the probe), and two different polymers (components 2 and 3) χ_{23} is generally different from χ_{32} since both polymers have different sizes. However,

$$\chi_{23}/V_2 = \chi_{32}/V_3 \quad (1)$$

where V_i is the molar volume of component i . This quantity is then independent of the number of segments in the polymer, and of the order in which polymers 2 and 3 are taken. In this review, we will use χ_{23}/V_2 values to compare data on polymer blends. Values in the literature are usually given as χ'_{23} or B , which are related to the above quantity in the following manner:

$$\chi'_{23}/V_3 = B/RT = \chi_{23}/V_2 \quad (2)$$

χ is a dimensionless parameter, whereas B has units of J cm^{-3}

MELTING POINT DEPRESSION

Using an expression first derived by Scott (3) for the chemical potential of binary mixtures, Nishi and Wang (4) described as follows the variation of the melting point of a semicrystalline polymer as a function of the composition of the polymer-polymer mixture

$$\frac{1}{T_m} - \frac{1}{T_m^0} = - \frac{R}{\Delta H_3} \frac{V_3}{V_2} \chi_{23} (1 - \phi_3)^2 \quad (3)$$

In Eq 3, T_m and T_m^0 are, respectively, the melting points of polymer 3 in the mixture and in the pure state, V_3 and ΔH_3 are the molar volume and heat of fusion of the pure crystalline component, V_2 the molar volume of component 2, and ϕ_3 the volume fraction of component 3. χ_{23} is the polymer-polymer interaction parameter per molecule of component 3 (1): we write χ_{23} instead of χ_{12} , which is normally given in the literature, simply to be consistent with the nomenclature used in the remainder of this paper when discussing other methods involving the use of a probe (vapor sorption and inverse-phase gas chromatography) where the probe will be component 1 and the two polymers, components 2 and 3.

From a series of differential-scanning calorimetry measurements, one can obtain the melting point of mixtures of different compositions, as shown in Fig. 1a for PEMA/PVF₂ blends (5), and calculate χ_{23} since

$$\frac{1}{\phi_2} \frac{\Delta T_m}{T_m} = - \frac{R}{\Delta H_3} \frac{V_3}{V_2} \frac{\phi_2}{T_m^0} \chi_{23} \quad (4)$$

where $\Delta T_m = T_m^0 - T_m$. Figure 1b shows that Eq 4 is obeyed for the PEMA/PVF₂ mixture, and it can therefore be concluded that the interaction parameter χ_{23} between PEMA and PVF₂ does not depend upon composition. We will see below that this is not a general situation.

Recent results obtained for various miscible blends using the melting point depression method are shown in Table 1. Values of χ_{23} are negative, indicating that for polymers with large molecular weights there is a negative enthalpy of mixing since their entropy of mixing can be considered to be zero.

Table 1 also indicates that the values of χ_{23} obtained for PMMA/PVF₂ blends by Morra and Stein (9) and Roerdink and Challa (10) are somewhat smaller than those of Nishi and Wang (4). These discrepancies can be interpreted as meaning that the values of χ_{23} determined from melting-point depression measurements depend upon the thermal history of the samples as suggested in the literature (1, 7, 9, 10).

Indeed, Aubin and Prud'homme (11) found that the melting points of PCL/CPVC blends cast from solution are higher than those of blends crystallized

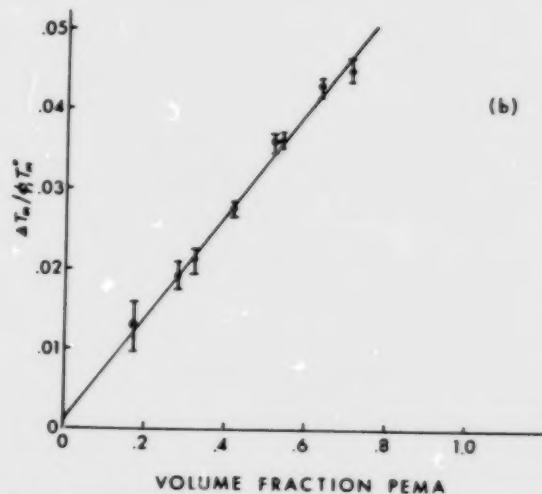
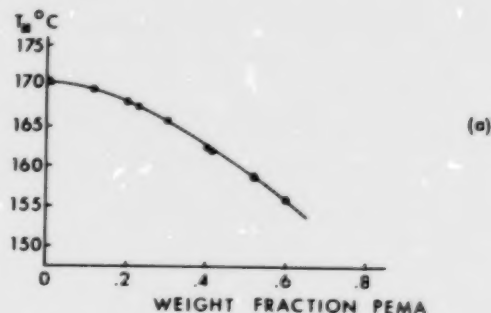


Fig. 1a. Melting point of PVF₂ in PEMA/PVF₂ blends as a function of PEMA weight fraction. Taken from Kwei, et al. (5).

Fig. 1b. Graphical method used to estimate χ_{23} from melting-point depression data for PEMA/PVF₂ blends. Taken from Kwei, et al. (5).

Table 1. Polymer-Polymer Interaction Parameters from the Melting-Point Depression Method.

Blend	χ_{23}	$\frac{\chi_{23}}{V_2} \times 10^{(4)}$ mol·cm ⁻³	T_m^0 /°C	Reference
Phenoxy/PBA	-1.04	-72	61	17
Phenoxy/PEA	-0.52	-44	49	17
Phenoxy/PCL	-0.42	-38	56	17
PEMA/PVF ₂	-0.13	-1.0	160	5
PEMA/PVF ₂	-0.08	-0.6	160	7
PMMA/PVF ₂	-0.29	-9.5	160	4
PMMA/PVF ₂ (50/50)	-0.12	-3.0	200	6
PMMA/PVF ₂ (α Form)	-0.20	-6.6	170	9
Isotactic PMMA/PVF ₂	-0.13	-0.8	175	10
Syndiotactic PMMA/PVF ₂	-0.06	-0.8	175	10
Atactic PMMA/PVF ₂	-0.10	-0.2	175	10
PVC/PMPL	-0.29	-4.9	90	11
PVC/PPL	-0.05	-0.8	250	11

* Calculated using χ_{23} values, densities and molecular weights cited by the various authors. V_2 is the volume of one polymer molecule, not of one segment. This remark also holds for Tables 2 and 4.

from the melt. Annealing of the latter samples leads to melting points equal to those found with solution cast samples, and, presumably, closer to equilibrium values.

Since the melting temperature of polymer blends is influenced both by kinetic and thermodynamic

factors, Morra and Stein (9) attempted to eliminate the kinetic factors. They constructed Hoffman-Weeks plots for PMMA/PVF₂ blends of various compositions and determined their equilibrium melting temperatures by extrapolation. These values correspond to the melting of crystals of infinite thickness and are therefore independent of thermal history (in general) and lamellar thickness (in particular). As mentioned above, they found negative values of χ_{23} (for the low temperature α Form of PVF₂) which are slightly lower than those reported by other authors (Table I).

Curvature in a plot such as in Fig. 1b would indicate a value of χ_{23} dependent on blend composition. This is, for example, seen in blends of PMMA/PVF₂, as is shown in Fig. 2, where χ_{23} is given as a function of the PVF₂ composition of the blend (6). Inverse-phase gas-chromatography measurements also show that χ_{23} is dependent upon composition in PMMA/PVF₂ blends (8) whereas values of χ_{23} reported by Nishi and Wang (4) are intermediate between the values of Fig. 2, as these authors did not find a significant variation of χ_{23} with composition.

The preceding examples indicate that the melting-point depression technique is a very valuable method for measuring the interaction parameter χ_{23} . It has the advantage of not involving the use of a probe nor disrupting the polymer-polymer interaction, contrary to most other methods suggested in the literature. However, it gives the interaction parameter χ_{23} only at one temperature, which is an important limiting factor.

VAPOR SORPTION

Vapor sorption is another phenomenon from which polymer-polymer interaction parameters can

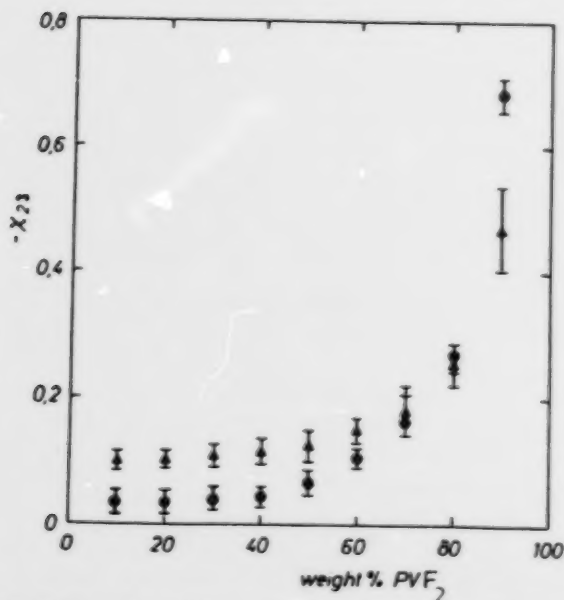


Fig. 2. Dependence of the interaction parameter χ_{23} from melting-point depression (Δ) and small-angle x-ray scattering ($\bullet$) for PMMA/PVF₂ blends at 200°C. Taken from Wendorff (6).

be calculated. This technique has been used for some time to characterize polymer-solvent interactions (12, 13). It involves measuring the amount of solvent vapor retained at equilibrium by a polymer sample.

From Scott's treatment (3), the activity, a_1 , of the solvent in a solvent (component 1)/polymer (component 2) solution is given by

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi_{12} \phi_2^2 \quad (5)$$

where ϕ_i is the volume fraction of component i . For a polymer blend, χ_{23} can be obtained, at low concentrations of probe, from

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) + (\chi_{12} \phi_2 + \chi_{13} \phi_3) \cdot (1 - \phi_1) - \chi_{23} \phi_2 \phi_3 V_3/V_2 \quad (6)$$

Isotherms for the sorption of benzene, and the resulting χ_{12} values for benzene/PS and benzene/PVME mixtures, are shown in Figs. 3 and 4 (5). χ_{23} can be obtained from similar data on polymer blends.

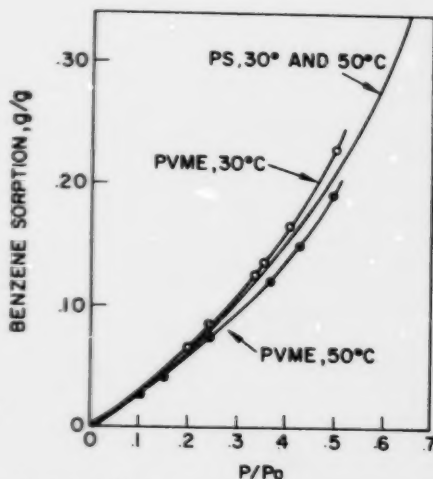


Fig. 3. Isotherms for the sorption of benzene vapor in PS and PVME. Taken from Nishi and Wang (37).

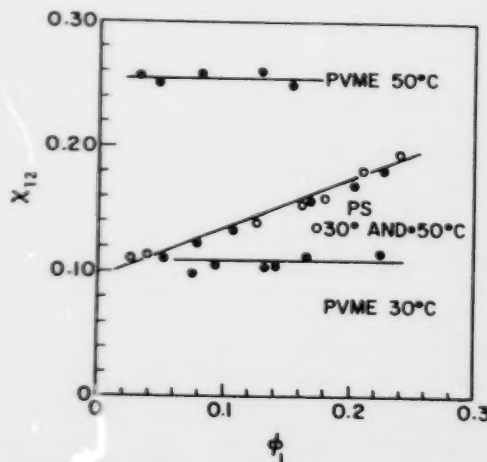


Fig. 4. Dependence of χ_{12} on benzene volume fraction for PS or PVME mixtures (gas sorption). Taken from Nishi and Wang (37).

Results of Kwei, *et al.* (5) for PS/PVME blends are shown in Table 2. The values of χ_{23} , which are composition and temperature dependent, are negative in accord with the observed miscibility of this mixture. In addition, the temperature dependence of the interaction parameter enabled these authors to predict both upper and lower cloud points at various compositions.

Also featured in Table 2 are some recent results obtained on PPO/PS and PC/CDTI blends, using CO₂ as a probe (14, 15). Along with the χ_{23} results, the diffusion process of the probe in the blend can also be described by assuming a Langmuir-type sorption mechanism.

Some workers suggested a dynamic version of this method. It consists in coating a piezo-electric crystal with a polymer or a polymer mixture and measuring changes in the resonant frequency of the crystal with solvent sorption. Results are therefore obtained much faster and are comparable with those of static measurements (16). Preliminary results on Phenoxy blends were published recently by Harris, *et al.* (17) but these are the only examples presently available in the area of polymer blends (Table 2), using this latest technique.

INVERSE-PHASE GAS CHROMATOGRAPHY

Inverse-phase gas chromatography (IPGC) (18) has often been used to investigate interactions between a probe, typically a small volatile molecule, and a liquid immobile phase like a long chain alkane (19). This method can be extended to investigate probe-polymer interactions (20), polymer-polymer interactions (21, 22), as well as plastifier-polymer (22, 23) and plastifier-plastifier interactions (22).

Given an inert carrier gas, a volatile probe present in small concentration as a vapor, and an immobile polymer liquid phase coated on an inert solid support, the interaction parameter at infinite dilution between the vapor and the immobile phase is given by (20)

$$\chi_{12} = \ln \frac{273.2 R v_2}{P_1^0 V_g^0 V_1} - \left(1 - \frac{V_1}{V_2}\right) - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (7)$$

where v_2 and V_2 are, respectively, the specific vol-

ume and molar volume of the polymer, P_1^0 the vapor pressure of the probe in the column, V_g^0 the specific retention volume of the probe, V_1 its molar volume, and B_{11} its second virial coefficient in the vapor phase. In this method, the specific retention volume is the experimentally important variable. It is equal to the volume of inert gas, measured at 273.2 K and corrected for column pressure drop, which will elute the vapor probe from a column containing 1 gram of stationary phase at temperature T .

Equation 7 enables calculation of χ_{12} and χ_{13} . In a similar fashion, $\chi_{1(23)}$, the interaction parameter between the probe and the polymer blend, is given by:

$$\chi_{1(23)} = \left(\frac{273.2 R (w_2 v_2 + w_3 v_3)}{V_g^0 P_1^0 V_1} \right) - \left(1 - \frac{V_1}{V_2}\right) \phi_2 - \left(1 - \frac{V_1}{V_3}\right) \phi_3 - P_1^0 \frac{(B_{11} - V_1)}{RT} \quad (8)$$

where w_2 and w_3 refer to the weight fraction of polymers 2 and 3, respectively, and v_3 is the specific volume of polymer 3. The polymer-polymer interaction parameter χ_{23} is then calculated from (22):

$$\chi_{1(23)} = \phi_2 \chi_{12} + \phi_3 \chi_{13} - \phi_2 \phi_3 \chi_{23} V_3 / V_2 \quad (9)$$

Since excellent reviews of this method were written by Guillet (18), and Gray (24), we will limit ourselves to a discussion of the influence of the probe upon χ_{23} and the analysis of some recent measurements.

Figure 5 shows the composition dependence of V_g^0 for two probes (acetophenone and 1-chlorooctane) in PMMA/PVF₂ blends (8). From values of V_g^0 , the parameters χ_{12} and χ_{13} (for probe/pure polymer systems) and $\chi_{1(23)}$ (for probe/polymer blend systems) were calculated, leading to χ_{23} , the polymer/polymer interaction parameter (Eq. 9). Variation of V_g^0 with composition is seen to be monotonous but not linear. Table 3 shows the values of χ_{23} corresponding to some of these values of V_g^0 . All values are negative at high PVF₂ contents, which is evidence for a negative heat of mixing between the two polymers and which is consistent with the melting-point depression data of Nishi and Wang (4).

Average χ_{23} values, calculated for a series of probes, can therefore be used, as shown in Fig. 6

Table 2. Polymer-Polymer Interaction Parameters from the Vapor Sorption Method.

A/B Blend	% of A in Blend*	χ_{23}	$\frac{\chi_{23}}{V_2} \times 10^6$ mol cm ⁻³	T/°C	Reference
PS/PVME	35	-0.75	-4.5	30	36
PS/PVME	45	-0.69	-4.1	30	36
PS/PVME	45	-0.60	-3.4	50	36
PC/CDTI	—	0.00	-97	35	15
PPO/PS	—	-1.08	-1.8	35	14
Phenoxy/PEA	—	-0.21	-11	55	17
Phenoxy/PBA	—	-0.89	-47	55	17
Phenoxy/PCL	—	-1.01	-53	55	17
Phenoxy/PCDS	—	-0.76	-39	55	17

* Some authors do not mention the composition corresponding to the value of χ_{23} reported. This value is then taken as composition independent.

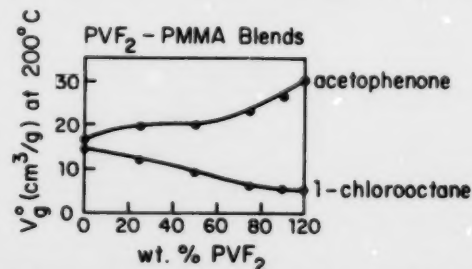


Fig. 5. Composition dependence of V_g^0 for two probes in PMMA/PVF₂ blends at 200°C by IPGC (8).

Table 3. Polymer-Polymer Interaction Parameters by Inverse-Phase Gas Chromatography.

Probe	A/B Blend	% of A in Blend*	T/°C	χ_{23}	Reference
Acetophenone	PMMA/PVF ₂	25	200	0.22	8
"	PMMA/PVF ₂	50	200	-0.05	8
"	PMMA/PVF ₂	75	200	-0.20	8
"	PMMA/PVF ₂	90	200	-0.28	8
Cyclohexanol	PMMA/PVF ₂	25	200	0.01	8
"	PMMA/PVF ₂	50	200	-0.01	8
"	PMMA/PVF ₂	75	200	-0.18	8
"	PMMA/PVF ₂	90	200	-0.22	8
Chloroform	PEMA/CPE	75	80	-0.32	27
"	PEMA/CPE	50	80	-0.22	27
"	PEMA/CPE	25	80	-0.44	27
"	PEMA/CPE	25	100	-0.14	27
"	PEMA/CPE	25	120	-0.22	27

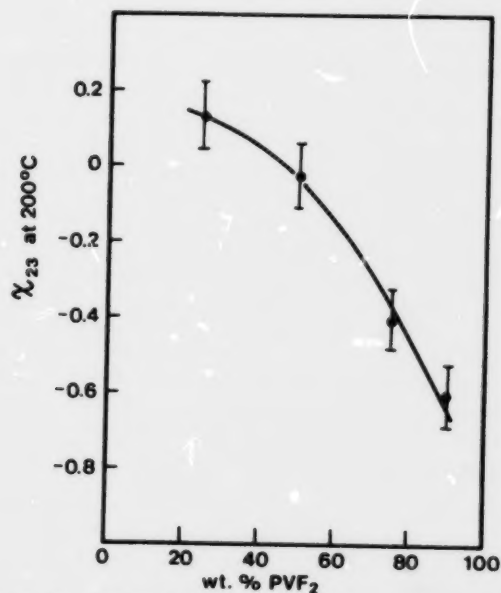


Fig. 6. Composition dependence of the polymer-polymer interaction parameter χ_{23} for PVF₂/PMMA blends at 200°C by IPGC. Taken from DiPaola-Baranyi, Fletcher, and Degré (8).

for PMMA/PVF₂ blends as a function of composition (8). These values agree reasonably well with those determined by Wendorff (6) from melting-point depression and small-angle x-ray scattering measurements (Fig. 2), except at low concentrations of PVF₂ where the IPGC method gives slightly positive values contrary to the two other methods. The reasons for this discrepancy have not yet been explained.

Often, values of χ_{23} determined by IPGC vary slightly with the probe selected (see the difference between the χ_{23} values measured with acetophenone or cyclohexanol in PMMA/PVF₂ blends (Table 3)). However, this variation may not be characteristic of IPGC. Careful measurements of χ_{12} between different solvents and PDMS by IGCC and vapor sorption (25) show a good agreement between the values determined by the two methods; it is probable, although we are not aware of such studies,

that vapor sorption measurements would lead to the same variation of χ_{23} with the probe used as seen with IPGC.

The variation of the results shown in Table 3 may thus reflect the tendency of the probe to partition between the two polymers, even if they are miscible, and the inadequacy of the Flory-Huggins theory to take into account such partition (26).

Values of χ_{23} for CPE/PBA blends are plotted in Fig. 7 as a function of volume fraction of CPE (27). The fluctuations observed are due to differences in polymer coating thickness and uniformity, and errors in the evaluation of column loading (27, 28). They indicate that a good precision of most experimental parameters, including V_g , is required in order to obtain precise χ_{23} values.

Zhikuan and Walsh (27) also noticed that there is a difference in the retention volumes (and in χ_{23} values derived from those) of homogeneous and phase-separated blends. It is well known that some mixtures, i.e. PS/PVME blends, phase separate depending upon the solvent from which they are cast and upon heating. These phenomena may well be a source of the discrepancies between measurements of different authors on the same blends (28).

Although column preparation is time consuming in IPGC, once the values of χ_{12} for different polymers are evaluated, one can rapidly proceed to blends of different compositions and obtain χ_{23} . In view of the aforementioned variations, such data are to be used with caution, but can be quite meaningful, especially for a systematic evaluation of variations of χ_{23} between a homopolymer and a homologous series of polymers.

NEUTRON SCATTERING

Small-angle neutron scattering (SANS) permits determination of the bulk values of χ_{23} , second virial coefficients, and chain dimensions (29-31).

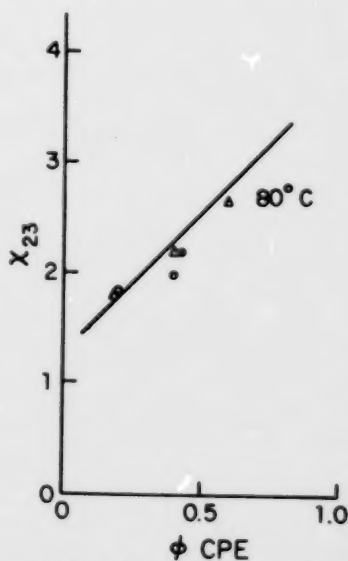


Fig. 7. Apparent values of χ_{23} for the CPE/PBA blend at 80°C as a function of volume fraction of CPE (27).

The method requires the deuteration of a fraction of the polymer to increase its scattering cross-section. In a blend, the deuterated polymer then acts as a "solute" dispersed in a "solvent" composed of undeuterated molecules of the same kind and molecules of the second polymer. For immiscible blends, the size of polymer aggregates can be determined (32 to 34). However, this presupposes that polymer-deuterated polymer interactions are negligible, and such interactions indeed seem to be minimal, although high enough to show in cloud point curves (35).

One benefit of this method has been to show that chain dimensions in bulk amorphous polymers and in miscible blends are the same and this offers an unambiguous way of determining polymer miscibility (33, 34).

The basic scattering relationship is

$$\frac{Kc}{R(s)} = \frac{1}{M P(s)} + 2 A_2 c \quad (10)$$

where $R(s)$ is the Rayleigh ratio, $P(s)$ the intermolecular interference function, $s = (4\pi\lambda \sin \theta/2)$, where θ is the scattering angle, λ the wavelength of the neutron radiation, K a constant, c the deuterated solute concentration, A_2 the second virial coefficient which is related to χ_{23} , and M the molecular weight of the deuterated polymer.

Values of χ_{23} are obtained by constructing a Zimm plot such as that of Fig. 8 (31). This method is of course reminiscent of the classical polymer-solution light-scattering technique. Equation 10 is the same in both cases, except for the constant K which is different.

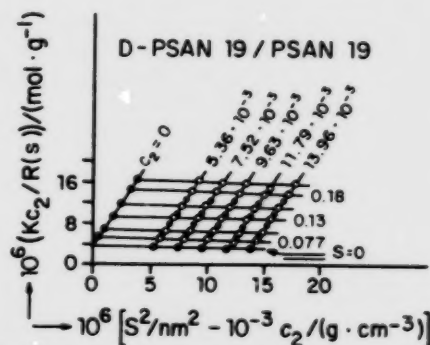


Fig. 8. Zimm plot from small-angle neutron-scattering data for the D-PSAN-19/PSAN-19 blend (31).

Results of various studies using SANS are summarised in Table 4. Hadziioannou, Stein, and Higgins (29) reported χ_{23} values for PS/PVME and PMMA/PVF₂ blends which agree well with values derived from melting point depression (PMMA/PVF₂, Table 1) or vapor sorption (PS/PVME, Table 2).

The SANS method was applied in a detailed way by Schmitt, *et al.* (31) not only to determine values of χ_{23} but also the enthalpic (χ_H) and excess entropic (χ_S) contributions to χ_{23} , for mixtures of PSAN at different compositions. In Table 4, the interaction parameter of 19-percent styrene poly(styrene-co-acrylonitrile) (PSAN-19) with its deuterated analogue is seen to be very small. This value agrees with that estimated by Yang, *et al.* (35) for PS/D-PS blends. D-PSAN-19/PSAN-19 blends show phase separation at high molecular weights and this is in agreement with the weakly positive χ_{23} values reported in Table 4. Mixtures of PSAN-19 with D-PMMA were also investigated (31): negative values of χ_{23} and χ_H were found, which is consistent with the miscibility of these blends. Unfortunately, a comparison with values obtained by other methods for mixtures of these copolymers is not yet possible.

The SANS method is free from the problems encountered with probes in vapor sorption and IGC methods, and in short, it appears to be quite promising despite the limited availability of the equipment required. It should be noted that it permits measurements at temperatures inferior to T_m and/or T_g , which are not possible with previous methods.

SMALL-ANGLE X-RAY SCATTERING

Small-angle x-ray scattering (SAXS) can also be used to determine χ_{23} . In this method, the ratio of the scattered intensity $I(s)$ to incident intensity I_0 is given by

$$I(s)/I_0 = I_e(1 + \cos^2 2\theta)/2 V S(s) \quad (11)$$

where I_e is the scattering factor of an electron, V the scattering volume, s the scattering vector, also used in Eq. 10, and λ the wavelength of the x-ray radiation. The value of $S(s)$, the scattering factor, is related to the chemical potential change of the components in the mixture and therefore to χ_{23} (6).

The total small-angle scattering of blends can be decomposed into a contribution independent of s

Table 4. Polymer-Polymer Interaction Parameters from Small-Angle Neutron Scattering.

A/B Blend	% A in blend	χ_{23}	$\frac{\chi_{23}}{V_2} \times 10^6$ mol cm ⁻³	$\frac{\chi_H}{V_2} \times 10^6$ mol cm ⁻³	$\frac{\chi_S}{V_2} \times 10^6$ mol cm ⁻³	T/°C	Reference
PS/PVME	25	-0.4	-4.4	—	—	25	29
PS/PVME	50	-0.3	-3.4	—	—	25	29
PMMA/PVF ₂	25	-0.3	-11.3**	—	—	25	29
PMMA/PVF ₂	50	-0.1	-3.1**	—	—	25	29
D-PSAN-19/PSAN-19*	—	0.4	2.2	—	—	25	31
D-PSAN-19/PSAN-20.5*	—	4.4	22	90	-68	25	31

* Number indicates the percent of acrylonitrile in the copolymer.

** Values calculated assuming a degree of crystallinity of 50 percent for PVF₂; densities taken from Ref. 40.

and a contribution which decays with increasing s . The first component can be attributed to particle density fluctuations at constant composition while the s -dependent component is due to concentration fluctuations at constant particle density. SAXS has recently been employed for the determination of χ_{23} in PMMA/PVF₂ blends (6, 37) in the molten state by analyzing the s -dependent contribution of $S(s)$ at various blend compositions. The result of this analysis is shown in Fig. 2, where the interaction parameter is plotted as a function of composition: good agreement is found with values derived from melting-point depression and IPGC, as we have said before. We are not aware of other measurements of this sort published in the literature.

DISCUSSION AND CONCLUSIONS

In general there is agreement between polymer-polymer interaction parameters measured through five different methods: melting-point depression, vapor sorption, inverse-phase gas chromatography, neutron scattering, and small-angle x-ray scattering. These methods are quite varied and each of them offers a number of advantages and disadvantages.

There is, however, some variation of the χ_{23} parameter, as can be seen through a comparison of the different values associated with the PMMA/PVF₂ blends in four of the five techniques reviewed. These variations may be due to peculiarities of the techniques used which are yet to be quantitatively accounted for and to the tendency of some authors to give an average χ_{23} parameter for the whole composition range of the blend, when one knows quite well that χ_{23} is composition dependent. In addition, the above comparison does not take into account variations of χ_{23} as a function of molecular weight, which are known to occur (38).

It should be noted that the melting-point depression method allows measurements of χ_{23} only at the melting temperature of the semicrystalline component of the blend; the inverse-phase gas chromatography method allows measurements of χ_{23} at temperatures above T_m for a crystalline blend, and above T_g for an amorphous blend, whereas the scattering techniques allow measurements over a wide range of composition and temperature, above or below T_m and T_g .

In this review, we have taken the χ_{23} parameter as a measure of the chemical interaction between the components of a blend. However, there can be an excess entropic contribution to χ_{23} , noted as χ_e . For blends of polymers with large molecular weights, the value of χ_e is small (3, 9). However, if the overall value of χ_{23} is also small, then χ_e can contribute significantly to χ_{23} as shown in Table 4.

Also, corrections have not been made for free-volume dissimilarity between the two polymers in the blend. This contribution to χ_{23} , which can be calculated with "equation of state" relationships, is always positive and varies from about 0.2 to 0.7 (1). Thus, a small positive value of χ_{23} may yield a negative value, more representative of polymer-polymer interaction, if the free-volume correction were made.

The value of χ_{23} may finally be influenced by other nonchemical factors such as molecular order enhancement or steric hindrance, which are yet to be quantitatively accounted for (39).

ACKNOWLEDGMENTS

The authors thank Professor Donald D. Patterson, of McGill University, for valuable suggestions in writing this paper. They also thank the National Sciences and Engineering Research Council of Canada and the Department of Education (FCAC program) of the Province of Québec for support of this work.

REFERENCES

- O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York (1970).
- R. Koningsveld and L. A. Kleintjens, *J. Polym. Sci., Polym. Symp.*, **61**, 221 (1977).
- R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).
- T. Nishi and T. T. Wang, *Macromolecules*, **8**, 909 (1975).
- T. K. Kwei, G. D. Patterson, and T. T. Wang, *Macromolecules*, **9**, 780 (1976).
- J. H. Wendorff, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 439 (1980).
- R. L. Imken, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.*, **16**, 593 (1976).
- G. DiPaola-Baranyi, S. J. Fletcher, and P. Degre, *Macromolecules*, **15**, 885 (1982).
- B. S. Morra and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 2243 (1982).
- E. Roerdink and G. Challa, *Polymer*, **19**, 173 (1978).
- M. Aubin and R. E. Prud'homme, *Macromolecules*, **13**, 365 (1980).
- R. D. Newman and J. M. Prausnitz, *J. Phys. Chem.*, **76**, 1492 (1972).
- O. Smidsrod and J. G. Guillet, *Macromolecules*, **2**, 272 (1969).
- G. Morel and D. R. Paul, *J. Membrane Sci.*, **10**, 273 (1982).
- P. Masi, D. R. Paul, and J. W. Barlow, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 15 (1982).
- S. Saeki and D. C. Bonner, *Polymer*, **19**, 319 (1978).
- J. E. Harris, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.*, **23**, 676 (1983).
- J. E. Guillet in "Progress in Gas Chromatography," (J. H. Purnell, Ed.), p. 187 Wiley-Interscience, N.Y. (1973).
- Y. B. Tewari, D. E. Matire, and J. P. Sheridan, *J. Phys. Chem.*, **74**, 2345 (1970).
- D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, *Macromolecules*, **4**, 356 (1971).
- O. Olabisi, *Macromolecules*, **8**, 316 (1975).
- D. D. Deshpande, D. Patterson, H. P. Schreiber, and C. S. Su, *Macromolecules*, **1**, 530 (1974).
- C. S. Su, D. Patterson, and H. P. Schreiber, *J. Appl. Polym. Sci.*, **20**, 1025 (1976).
- D. G. Gray, *Progress Polym. Sci.*, **5**, 1 (1977).
- W. R. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, **5**, 12 (1972).
- D. J. Walsh and J. C. McKeown, *Polymer*, **21**, 1335 (1980).
- C. Zhikuan and D. J. Walsh, *Eur. Polym. J.*, **19**, 519 (1983).
- R. N. Lichtentaler, R. E. Newman, and J. M. Prausnitz, *Macromolecules*, **6**, 650 (1973).
- G. Hadzioannou, R. Stein, and J. Higgins, *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.*, **24**, 213 (1983).
- R. P. Kambour, R. C. Bopp, A. McConnachie, and W. J. MacKnight, *Polymer*, **21**, 133 (1980).
- B. J. Schmitt, R. G. Kirste, and J. Jelenic, *Makro. Chem.*, **181**, 1655 (1980).
- D. J. Walsh, J. S. Higgins, and J. C. McKeown, *Polymer*, **22**, 168 (1981).
- D. G. H. Ballard, M. G. Rayner, and J. Schelten, *Polymer*, **17**, 640 (1976).
- G. D. Wignall, H. R. Child, and F. Li-Aravena, *Polymer*, **21**, 131 (1980).

35. H. Yang, G. Hadziioannou, and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 159 (1983).
36. T. K. Kwei, T. Nishi, and R. F. Roberts, *Macromolecules*, **7**, 667 (1974).
37. J. H. Wendorff, *Polymer*, **23**, 543 (1982).
38. T. K. Kwei and H. L. Frisch, *Macromolecules*, **11**, 1267 (1978).
39. M. Barbe and D. Patterson, *J. Phys. Chem.*, **82**, 40 (1978).
40. D. W. Van Krevelen, "Properties of Polymers: Their Estimation and Correlation with Molecular Structure," 2nd ed., Elsevier, Amsterdam, (1976).

Nomenclature

CDTI	= Poly(1,4-cyclohexane dimethanol-co-terephthalic acid-co-isophthalic acid)
CPE	= Chlorinated poly(ethylene)
CPVC	= Chlorinated poly(vinyl chloride)
PMPL	= Poly(α -methyl- α -n-propyl- β -propiolactone)
PBA	= Poly(1,4-butylene adipate)
PC	= Poly(carbonate of Bisphenol A)
PCL	= Poly(ϵ -caprolactone)
PCDS	= Poly(1,4-cyclohexane dimethanol succinate)
PDMS	= Poly(dimethyl siloxane)
PEA	= Poly(ethylene adipate)
PEMA	= Poly(ethyl methacrylate)
PHENOXY	= Poly(hydroxyether of Bisphenol A)
PMMA	= Poly(methyl methacrylate)
PPO	= Poly(phenylene oxide)
PPL	= Poly(pivalolactone)
PS	= Poly(styrene)
D-PS	= Deuterated poly(styrene)
PSAN	= Poly(styrene-co-acrylonitrile)
D-PSAN	= Deuterated poly(styrene-co-acrylonitrile)
PVC	= Poly(vinyl chloride)
PVF ₂	= Poly(vinylidene chloride)
PVME	= Poly(vinyl methyl ether)

DISCUSSION

L. A. Utracki: Here, in the Industrial Materials Research Institute, we are forced to look into applications of what we learn from more fundamental studies. I would appreciate it if you could draw some conclusions on the usefulness of χ_{23} evaluated via these five methods. For instance, can we use these to calculate the phase equilibria in polymeric systems. You rated very highly what I would call solid-state methods: SAXS AND SANS. However, how useful is this information in calculating the phase-equilibrium condition during the melt processing, even assuming perfect steady-state morphology, orientation, or process condition?

B. Riedl: Four of the methods described in this paper (melting-point depression, inverse-phase gas chromatography, SAXS, and SANS) allow the measurement of χ_{23} in the melt where equilibrium can be achieved. However, three methods (vapor sorption, SAXS, and SANS) give χ_{23} values in the solid state where equilibrium is not easily reached. In the latter case the measurement of χ_{23} is certainly influenced by nonequilibrium states, as any other measurements made on these systems.

P. Zoller: Is there any hope that one can get any meaningful number for, let us say, the temperature dependence of χ_{23} out of measuring in the solid state? Being a nonequilibrium situation, can one assume at all that the T -dependence of χ_{23} in the glass will be anywhere close to the equilibrium? Then, one has the χ -parameter dependent on temperature, pressure composition, and everything else. One has to mention what is the usefulness of this elaborately determined functions.

B. Riedl: To my knowledge, measurements of χ_{23} as a function of temperature have not been made yet in the solid state. It must be realized that samples analyzed in the solid state can give information about the conditions from which they were prepared. Their analysis as a function of temperature may not be that useful, but the analysis in the solid state of samples quenched from melts (at different temperatures) may be interesting.

P. Zoller: One draws a lot of conclusions taking χ_{23} determined in solid state at one temperature, then in solution at another one. How does the miscibility change with T ?

B. Riedl: It is true that the χ_{23} measurements currently available are scattered and a comparison of the same system, by different methods, can hardly be made. In that context, additional measurements are certainly necessary. Concerning the χ_{23} dependence as a function of T , measurements are available in Ref. 27 and in C. Herkt-Maetzky and J. Schelten, *Phys. Rev. Lett.*, **51**, 896 (1983).

P. Zoller: But as you said, χ_{23} depends on everything you can think of. What is the usefulness of it? The results you presented look terrible. When you compare the values determined by different methods you get tremendous differences: variation of χ_{23} from zero to minus one is a world of difference.

B. Riedl: The lack of agreement between values of χ_{23} as measured by different techniques may be due to the different thermal histories of the samples (in the solid state), to differences in molecular weight, temperature, and composition of the blend: what we are saying is that χ_{23} does depend on these factors.

P. Zoller: Could you name one useful application of χ_{23} when it varies with method of measurements in such a wide range? Can you tell us what will be the variation of the critical point if χ_{23} varies by unity?

H. P. Schreiber: If you use a single technique, e.g. the inversed gas chromatography, with which I am more familiar than with the others, then one gets a molecular, or atomic estimate, on the miscibility in a given 2-3 component. As far as the thermodynamics are concerned, or as far as a group of probes are concerned, they see the equilibrium truth. But there is a difficulty in using χ_{23} determined by this technique to rationalize or predict bulk properties in a polymer blend. One of the main reasons for this problem is that when people assess the mechanical or melt properties of a multicomponent system they hardly ever measure these in a steady state. One always questions the validity of measurements in a nonequilibrium state. It seems that the only true usefulness of χ_{23} is to predict whether or

not over a long span of time, a given system will retain its properties, or whether, because of nonequilibrium, these properties will shift.

R. Simha: I want to add something, or rather go back to Dr. Utracki's question: what prediction can you extract from the measurements of χ_{23} ? He asked if you can get information regarding phase equilibria. Well, it is not the situation as such since this would require an adequate theory or detailed data. In order to predict phase equilibria, one has to know the compositional derivatives for which one has to know the χ_{23} function very well. I think that you do not know it. Furthermore, the theory does not exist that would allow you to calculate the phase equilibria.

R. E. Prud'homme: I would like to respond briefly to the comments made by Dr. Zoller. It is important to realize that a comparison has been made between five methods which are drastically different. In the review presented by Dr. Riedl, scattering methods as well as equilibrium methods have been used to

measure χ_{23} . In view of the conceptual differences between these methods, in view also of the different experimental conditions given in the literature, it is not surprising to find some disagreement between the values reported for a given system. However, the χ_{23} values can still be used to compare a series of systems, particularly in the melt state. I think that Dr. Riedl has shown some examples of this sort. He has also shown that all five methods are not equally useful and universal. Depending upon the problem investigated, one method may be preferred to another.

A. A. Alim: Let us go down to practical aspects. In the first method you discussed (melting-point depression), down to what temperature differences is it useful?

B. Riedl: Down to 2 to 3°C as indicated in the quoted literature, e.g. for PMMA/PVF₂ (4, 9). In typical blends, melting-point depressions of the order of 10 to 15 degrees are recorded, sometimes more, sometimes less.

Compatibilization of Polyester/Polyamide Blends via Catalytic Ester-Amide Interchange Reaction

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In a series of publications we reported on melt rheology, morphology, and mechanical properties of the poly(ethylene terephthalate)/poly(amide-6,6) blends (PET/PA). The non-oriented samples had poor interphase bonding resulting in low impact and tensile strengths. To improve these properties the ester-amide interchange reaction was carried out in solution and in melt. In the latter case a Brabender Plastograph was used in the mixing chamber or twin-screw extruder configurations with p-toluenesulfonic acid as a catalyst. The interchange reaction was followed by 400 MHz proton and ^{13}C nuclear magnetic resonance spectroscopy.

INTRODUCTION

Although significant progress has been made in the understanding of the interchange reactions in polyester-polyester and polyamide-polyamide systems, there is a lack of information concerning the reactions between polyamide-polyester. A general review of these reactions was recently published by Katliar [1] and their applications in formation of block polymers are briefly covered by Allport, *et al.* [2] and Noshay, *et al.* [3]. There is considerable uncertainty about the mechanism involved, as well as the role that water plays in the process.

The polyesteramides were the subject of extensive investigations in recent years. The main interest has been focused on polyesteramides obtained by polycondensation of monomeric hydroxyamido acids or aminoalcohols with diacid chlorides [4 to 14]. Some attention has been devoted specifically to modifications of poly(ethylene terephthalate) (PET), leading to polyesteramides [15 to 18]. These copolymers are of commercial interest due to their good fiber-forming properties.

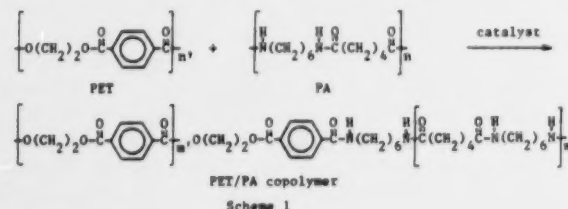
In this work we shall focus on PET modification by ester-amide interchange reactions, and its effect on PET/poly(amide-6,6) (PA) compatibility, hopefully leading to improvements in the mechanical properties of the blends.

Utracki, *et al.* [19 to 22] have studied the melt rheology of blends of PET and PA and their results indicated the presence of a degree of association and/or cocrystallization involving these two polymers. Recently Kamal, *et al.* [23] have reported that PET and PA exhibit a certain degree of compatibility in the molten state, but the blends show brittle failure in both tensile and impact tests. For these

tests the samples were obtained by molding in a reciprocating-screw injection-molding machine. Due to the brittleness the nonoriented blends would not be very useful in applications where the mechanical properties are important. The brittleness originates in a poor interphase of the PET/PA system. On crystallization there is a physical separation of the phases to the extent that microtoming pulls the dispersed PA phase out of the PET matrix.

The literature search shows that blending of PET and PA in the melt produces polyester-polyamide block polymers. These studies are reported mostly in the patent literature [24 to 29]. The structures of the products have not been reported. The reactions have been conducted at 220 to 290°C under reduced pressure for 5 to 30 hours without any catalyst. Only one reference was found on the catalytic PET/PA interchange reaction. Inoshita, *et al.* [29] reported that heating a mixture of these polymers in the presence of zinc acetate and antimony trioxide, at 230 to 280°C under 0.01 torr for 5h results in the formation of a block polymer. This seems to be too long for an industrial process.

It would be desirable to develop a method of a catalytic ester-amide interchange reaction to take place during the regular processing step, i.e., extrusion or blowmolding operations. It is proposed that the following Scheme 1 be considered.



By controlling the reaction conditions one would expect to be able to adjust the extent of the interchange during the processing (extrusion or injection/blowmolding). Such a control should allow for the variation in the degree of dispersion of PA in PET, prevent the phase-ripening and improve the mechanical properties of the blends.

In the literature there are only a few examples of the catalytic ester-amide interchange in a polyester/polyamide system (other than PET/PA). Korshak, *et al.* [30 and 31] have reported the interchange reaction between polyamides and polyesters in the presence of 1 percent PbO [30] or 2 percent PbO₂ [31]. Copolymers were obtained by heating at 260°C for 3 to 8 h. Another example of an ester-amide interchange reaction catalyst was reported by Frunze, *et al.* [32]. They applied iso-Bu₃Al as a catalyst to obtain a ϵ -caprolactam- ϵ -caprolactone copolymer. The use of this catalyst is limited only to reactions carried out in solution (commercially available as a solution in toluene).

It is obvious that in order to accomplish the task, one has to find an efficient catalyst. It was decided to use p-toluenesulfonic acid (TsOH). This compound is known as a good catalyst for the ester-ester exchange reaction [33] as well as for the condensation reaction of PA with the carbonyl group of formaldehyde [34]. Commercially available TsOH is inexpensive, stable and easy to handle (white solid, T_m = 105°C).

EXPERIMENTAL

Kodapak 7352 (supplied by Eastman Kodak) and Zytel 42 (supplied by E.I. DuPont de Nemours and Co.) were the PET and PA resins, respectively, employed in this study. Their properties are listed in Table 1.

Prior to blending the material was dried: PET at 135°C and PA at 85°C for 72 h under reduced pressure. The dried resins, combined in the desired proportions were mixed with 0.2 percent (by weight) of TsOH (practical grade, supplied by Eastman Kodak Co.). The reaction was carried out under nitrogen either in the mixing chamber of a Brabender-Plastograph (Table 2) or in the twin-screw extruder (Table 3). The structures of the resulting materials were analyzed by means of the high resolution ¹H and ¹³C nuclear magnetic resonance, ¹HNMR and ¹³CNMR, respectively. The spectra were measured with a Bruker 400 FT-NMR spectrometer with a magnetic field strength of 9.4 Tesla (*e.g.*, ¹H = 400 MHz; ¹³C = 100.6 MHz). The samples were dissolved at 40 to 50°C in a 2 to 1

(by volume) mixture of trifluoroacetic acid (TFA) and deuterated chloroform (CDCl₃). The solutions were kept at the same temperature during the testing. The equimolar PET/PA blends (Tables 2 and 3) were prepared only in order to facilitate interpretation of NMR data.

RESULTS

The literature review showed that ¹HNMR and ¹³CNMR spectroscopy is a useful tool for the analysis of various polyesteramides prepared by the polycondensation reaction of corresponding monomers [13 and 14]. It was decided to use this method in order to calculate the extent of the interchange reaction between PET and PA.

Prior to analysis of the blends it was necessary to carry out the spectroscopic characterization of the neat resin. The PA was found to be a pure, regular polymer. Conversely the 400.13 MHz ¹HNMR spectrum of PET (Fig. 1) displayed three aromatic signals (*x*, *y*, *z*) and four peaks (*a*, *b*, *c*, *d*) for the aliphatic protons. For strictly regular PET one would expect only one aliphatic peak (*a*) and one aromatic peak (*x*). In general the aromatic protons are useful for the sequence analysis. The aliphatic ones allow detection of self-condensation products of the ethylene glycol during PET polymerization leading to di- and triethylene glycol blocks. These side reaction products are responsible for the *b*, *c* peaks (diethylene glycol) and *b*, *c*, *d* peaks (triethylene glycol) (Scheme 2). The integration shows the presence of 5.1 percent of triethylene glycol and/or diethylene glycol units in the commercial PET.

Similarly, the 100.62 MHz ¹³CNMR spectrum shows additional peaks of carbons of triethylene and/or diethylene glycol units in PET (Fig. 2), supporting the above conclusions. However, the ¹³CNMR does not show the expected additional peak of the carbonyl group adjacent to the triethylene or diethylene glycol units. The aromatic pro-

Table 2. Conditions and Compositions of PET/PA Blends Mixed in a Brabender - Plastograph.

Material Code	Composition		Reaction Conditions		
	PA (wt.%)	TsOH (wt.%)	Temp. (°C)	Speed ^a (rpm)	Time (min)
1B	10	0.2	265	91	25
2B	0	0.2	295	91	10
3B	10	0.2	295	91	10
4B	54.1 ^a	0.2	295	91	35

^a Equimolar ratio of PET and PA.

^b Speed of mixing blades.

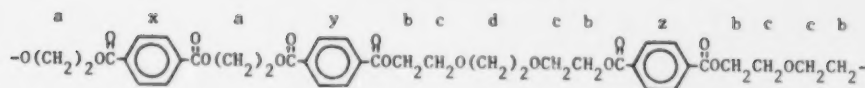
Table 3. Extrusion Conditions for Equimolar PET/PA Blends.

Material Code	TsOH (wt.%)	Speed ^a (rpm)	Extruder Parameters		Residence Time (min)
			Temperature (°C) Barrel	Die	
1E	0.2	21	350/360/370	361-363	2
2E	0.2	21	310/320/330	319-321	2
3E	0.2	10	305/315/325	314-315	4
4E	0	10	310/320/330	320-321	4
5E	0.2	10	290/300/310	301-303	4

Note: screw speed in rpm

Table 1. Properties of Pure Materials as Quoted in Commercial Literature.

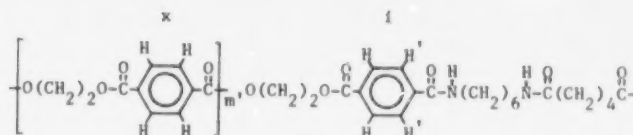
Commercial Name, Symbol	M _w	M _w /M _n	Melting Point		Melt Viscosity at 275°C (poise)
			T _m (°C)	Softening Point (°C)	
Kodapak 7352 (PET)	55,000	2.2	257	245	—
Zytel 42 (PA)	36,000	—	258	—	25,000



Scheme 2

tons in the ^1H NMR seem to be more sensitive to sequence effects than carbons in ^{13}C NMR.

For all the blends listed in Tables 2 and 3 both ^1H NMR and ^{13}C NMR spectra were run. The extent of the interchange reaction was calculated using ^1H NMR spectra since, as indicated above, the aromatic protons were more sensitive to sequence analysis than carbons in the PET unit. To calculate the extent of the reaction we refer to Scheme 3.

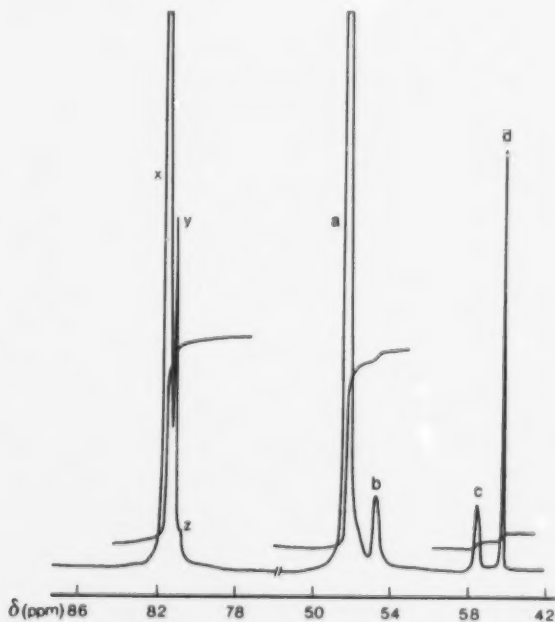


Scheme 3

The substitution of one ester group in the PET unit by an amide group of PA changes the chemical shift of the aromatic protons, in addition to the y and x shifts discussed before. Integrating this additional peak (i) separately and referring its magnitude to the total integral of aromatic protons, the following equation can be written:

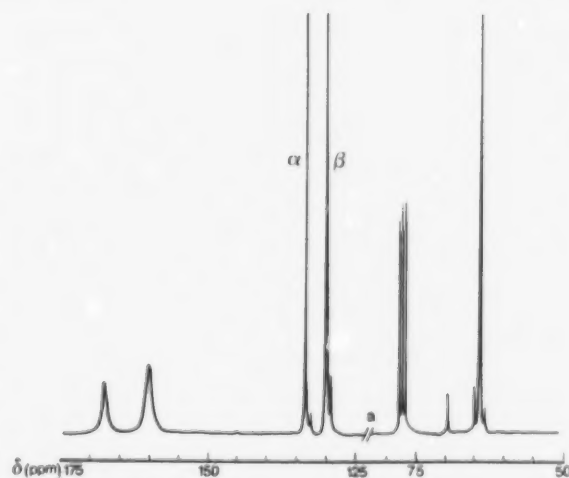
$$Y = 100I_i/I_j \quad j = x, y, z, i$$

where Y is the extent of the interchange reaction (in percent), and I_j indicates the peak integrals. The values of Y for the blends listed in Tables 2 and 3 are given in Table 4.

Fig. 1. 400.13 MHz ^1H NMR spectrum of PET.

peak (i) indicates the formation of polyesteramide. The extent of the reaction was calculated as $Y = 1.8$ percent. It is worth mentioning that the chemical shift difference between peaks x and i of 0.0523 ppm is observable only in 400 MHz ^1H NMR.

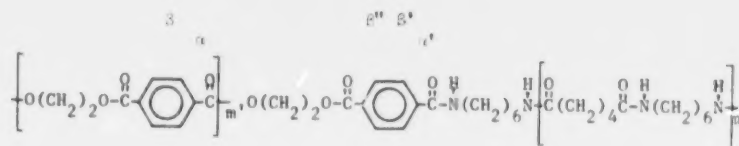
Blend 4B, which was prepared in equimolar monomer ratio was analyzed using both ^1H and ^{13}C NMR. The ^1H NMR spectrum shows the splitting

Fig. 2. 100.6 MHz ^{13}C NMR spectrum of PET.Table 4. Extent of the PET/PA Interchange Reaction as Calculated from ^1H NMR.

Material Code	1B	3B	4B	1E	2E	3E	4E	5E
Conversion	0	1.8	5.4	23.3	2.8	2.3	0	0
Conditions in Table*	2	2	2	3	3	3	3	3

* See Tables 2 and 3.

of the terephthaloyl signal from which 5.4 percent of the interchange-reaction product was calculated. The ^{13}C NMR spectrum also shows the presence of about 5 percent of the interchange-reaction product calculated from the intensity of the carbons of the aromatic ring (Scheme 4).



Scheme 4

The quaternary aromatic carbons (α) at 133.5513 ppm and the other carbons (β) at 130.0689 ppm show additional peaks at 133.8530 ppm (α') and 130.6156, 130.4466 ppm (β' , β''). The splitting of

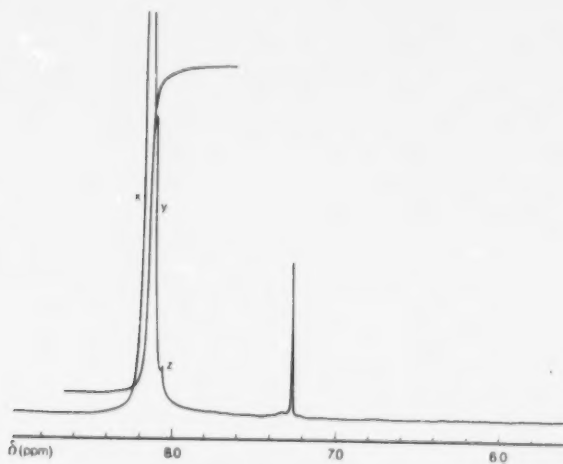


Fig. 3. 400.13 MHz ^1H NMR spectrum of PET/PA blend 1B (265°C, 25 min) — no interchange reaction.

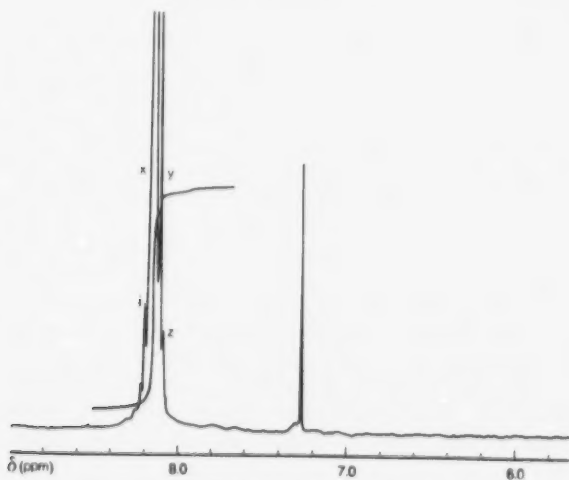


Fig. 4. 400.13 MHz ^1H NMR spectrum of PET/PA blend 3B (295°C, 10 min) — interchange reaction occurred ($Y = 1.8$ percent).

the α and β peaks is caused by the presence of the amide group in the para position to the ester group. As shown in Scheme 4 the substitution of the ester by the amide group affects the nearest quaternary carbon (α) as well as produces different chemical shifts of the two β -carbons [35].

In addition to the blends in the molten state (Tables 2 and 3) it was of interest to verify if the reaction would take place in solution. Poor mixing during melt blending can lead to significant concentration fluctuations between volume elements. In solution this variability is eliminated. However, the concentration of reactive species in solution is lower by several orders of magnitude, which should reduce the overall rate of reaction. PA (22.6g) was dissolved in 150mL of TFA during 1.5h of heating at 50 to 60°C with stirring. After dissolution of PA, PET (19.2g) was introduced and heated together for 1h until all PET was dissolved. After dissolution, the solution was poured into methanol, filtered, washed, and vacuum dried for 48h at 80°C. The recovered material (38g) was divided into two portions and each was mixed in a Brabender-Plastograph mixing chamber at 295°C for 10 min. To the first portion 0.2 percent of TsOH was added; the second part was blended without the catalyst. The ^1H NMR spectra were run for the three materials: PET/PA precipitated but not melt-blended, blended with TsOH, and without the catalyst. In the first case ^1H NMR showed a broadening of all peaks with regard to the unprecipitated blends. There were no indications of the interchange reaction. The broadening could be evidence of enhanced hydrogen bonding causing delay in chain mobility. The effect should be investigated further. In the second case the material was found to be susceptible to thermal degradation. After 10 min at 295°C it discolored (dark brown). The ^1H NMR indicated the degradation of PA. Finally, in the last case, mixing for up to 30 min did not produce either degradation or ester-amide interchange.

In conclusion, dissolution in TFA did not result in the ester-amide interchange reaction. The precipitated material, when blended in a Brabender-Plastograph mixing chamber without a catalyst, did not generate polyesteramide. There is a drastic, unexplained difference in behavior between the precipitated and nonprecipitated PET/PA blends in the presence of TsOH.

CONCLUSIONS

It was shown by both the ^1H and ^{13}C NMR that p-toluenesulfonic acid (TsOH) is an efficient catalyst

for the ester-amide interchange reaction in the PET/PA blend. It was also shown that the interchange ester-amide reaction can be accomplished during single pass of the catalyzed blend through an extruder. The reaction can be effectively accomplished during about 2 to 4 min of residence time in contrast with 6 to 30h of heating as described in the patent literature. However, further work is necessary in this area.

In order to transfer this information into a commercial operation, extensive studies of the effect of various processing conditions on $\bar{Y}$ are necessary. One has to have a kinetic description of the reaction in order to select the optimum conditions for industrial operation. Furthermore the molecular weight characterization, melt rheology, mechanical properties of oriented and nonoriented polyester-amides, as well as their stabilities must be investigated.

ACKNOWLEDGMENT

The help of Mr. François Hamel in operating of a Brabender-Plastograph is deeply appreciated.

REFERENCES

1. A. M. Kotliar, *J. Polym. Sci., Macromolec. Rev.*, **16**, 367 (1981).
2. D. C. Allport and W. H. Janes, "Block Copolymers", Applied Science Publishers, Barking, England, (1973).
3. A. Noshay and J. E. McGrath, "Block Copolymers", Academic, New York, N.Y. (1977).
4. T. M. Laakso and D. D. Reynolds, *J. Am. Chem. Soc.*, **82**, 3640 (1960).
5. J. L. R. Williams, T. M. Laakso, and L. E. Contois, *J. Polym. Sci.*, **61**, 353 (1962).
6. J. L. R. Williams, J. M. Carlson, and D. D. Reynolds, *Makromol. Chem.*, **65**, 54 (1963).
7. J. Preston, *J. Polym. Sci., A-1*, **8**, 3135 (1972).
8. G. Manzini, V. Crescenzi, A. Ciana, E. Ciceri, G. Della Fortuna, and L. Zotteri, *Eur. Polym. J.*, **9**, 941 (1973).
9. C. Borri, E. Sorta, and L. Zotteri, *Polymer*, **16**, 565 (1975).
10. M. Cesari, G. Perego, and A. Melis, *Eur. Polym. J.*, **12**, 585 (1976).
11. P. Akcatel and B. Jasse, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1537 (1976).
12. S. Katayama, T. Murakami, Y. Takahashi, H. Serita, Y. Obuchi, and T. Ito, *J. Appl. Polym. Sci.*, **20**, 975 (1976).
13. G. Della Fortuna, E. Oberrauch, T. Salvatori, E. Sorta, and M. Bruzzzone, *Polymer*, **18**, 269 (1977).
14. H. R. Kricheldorf and J. Kashig, *Eur. Polym. J.*, **14**, 923 (1978).
15. K. Ateya, *Angew. Makromol. Chem.*, **7**, 79 (1969).
16. K. Dimov and Y. Georgiew, *Angew. Makromol. Chem.*, **39**, 21 (1974).
17. J. M. Huet and E. Marechal, *Eur. Polym. J.*, **10**, 757 (1974).
18. I. F. Osipenko, G. L. Tsvilik, L. I. Mishkina, N. R. Prokopchuk, *Dokl. Akad. Nauk BSSR*, **27**, 918 (1983).
19. L. A. Utracki, G. L. Bata, *Am. Chem. Soc., Prepr. Org. Coatings Plastics Chem.*, **45**, 180 (1981).
20. L. A. Utracki and G. L. Bata, "Polymer Alloys III", D. Klemper and K. C. Frisch, Eds., Plenum Press, New York, N.Y. (1982).
21. L. A. Utracki, M. R. Kamal, V. Tan, A. Catani, and G. L. Bata, *J. Appl. Polym. Sci.*, **27**, 1913 (1982).
22. L. A. Utracki and G. L. Bata, *SPE ANTEC, Tech. Papers*, **28**, 84 (1982).
23. M. R. Kamal, M. A. Sahto, and L. A. Utracki, *Polym. Eng. Sci.*, **22**, 1127 (1982).
24. Firestone Tire and Rubber Co., *Neth. Pat. Appl.* 6,410,530 (1965); C.A., **63**:0153a (1965).
25. Toyo Rayon Co. Ltd., *Brit. Pat.*, 1,141,118 (1969); C.A., **70**:69220j (1969).
26. K. Okazaki and T. Nakagawa, *Japan Pat.*, 6911,669 (1969); C.A., **71**:103056t (1969).
27. T. Kiyotsukuri, *Kobunshi Kagaku*, **28**, 302 (1971); C.A., **75**:9891b (1971).
28. J. G. Martins and K. F. Ashley, *Ger. Offen.* 2,129,476 (1971); C.A., **76**:114155d (1972).
29. K. Inoshita, M. Terakawa, and T. Yasuda, *Japan Pat.*, 7228,916 (1972); C.A., **78**:3075x (1973).
30. V. V. Korshak, S. V. Vinogradova, M. M. Teplyakov, F. D. Fedorova, and G. Sh. Papava, *Vysokomol. Soedin.*, **8**, 2155 (1966).
31. V. V. Korshak, S. V. Vinogradova, M. M. Teplyakov, and A. D. Maksimov, *Izv. Vyssh. Uchebn. Zaved. Khim. i Khim. Technol.*, **10**, 688 (1967).
32. T. M. Frunze, V. V. Kurashov, L. B. Danilevskaya, B. A. Rozenberg, and V. V. Korshak, *Vysokomol. Soedin., Ser. A*, **16**, 1250 (1974).
33. M. Fieser and L. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley-Interscience, New York, (1966).
34. T. L. Cairns, H. D. Foster, A. W. Larchar, A. K. Schneider, and R. S. Schreiber, *J. Am. Chem. Soc.*, **71**, 651 (1949).
35. P. Solar, "Nuclear Magnetic Resonance Spectroscopy", Vol. 1-2, CRC Press, Inc., Boca Raton, FA, (1983).

DISCUSSION

A. Rudin: My comment is made mainly to solicit others. The blending of polyesters with polyamides was tried a long time before, e.g. to prevent flat spotting in Nylon-6,6 tire cords and for other applications. I have the impression that results have been rather disappointing. The reason given was that when one gets an exchange reaction one ends up with a shorter sequence length, particularly in a polyester. It seems that when the sequence length is too short one will not get the mechanical properties one may expect.

L. Z. Pillon: I agree. My next step is going to be molecular characterization of the reaction product from the point of view of the molecular weight, effects of degradation, variation of the sequence length, etc. If the chain length is too short we may have to look for another catalyst.

A. Rudin: I was not even talking about the molecular weight but of the polyester and polyamide sequence lengths in the copolymer.

L. Z. Pillon: I understand. Thank you.

R. P. Patel: Did you see any change in viscosity when mixing the blends? In particular in the presence of the catalyst?

L. Z. Pillon: Yes, the mixture after addition of the catalyst looked different; it was easier to mix.

R. P. Patel: Would that be because of a crosslinking reaction?

L. Z. Pillon: NMR spectra do not indicate any changes due to crosslinking. These would be easy to see by the NMR method, especially in 400 MHz ^1H and 100 MHz ^{13}C NMR spectra.

C. Sadr: Did you observe any change in MFI or melt strength?

L. Z. Pillon: The project started five months ago. In the first stage it was necessary to find the right catalyst for the ester-amide interchange reaction. The second stage was to prove that the reaction takes place. The molecular characterization, melt flow studies, and the mechanical tests will come later.

M. R. Kamal: I wonder if you had a chance to look at the microstructure of these blends prepared

without and with the catalyst. Is there any difference in the phase dispersion, interphase type . . . ?

L. Z. Pillon: We tried to look at the blends using the scanning electron microscope, but the study is far from finished. I have a few micrographs of the blends fractured under liquid nitrogen. Some of these I treated for 5 minutes with formic acid. The only difference I noticed was that polyamide was not as easy to remove (by acid treatment) from the catalyzed blends as from the blends prepared without a catalyst. In the latter case all polyamide was removed after 5 minutes of acid treatment whereas in the samples prepared with the catalyst treated in the same way I could see balls of polyamide dispersed in the PET matrix. The studies are being continued.

M. R. Kamal: But you did not look at the blends not treated with the formic acid?

L. Z. Pillon: Oh, yes. But I did not see any significant difference between samples with and without catalyst. The dispersions seem to be very similar, the interphase rather difficult to observe. The only time the difference was quite apparent was after the acid treatment.

L. A. Utracki: I would like to add one comment. It is true what Alf Rudin said about the disappointing

behavior of PET/PA blends as tire cords. The reduction of the PET sequence lengths is one reason, the degradation of PA during extrusion is another; there are dead spots in the extruder where PA accumulates, slowly degrades and causes a reduction of the melt strength of the spinned filaments. We have here a system where during a single pass through an extruder, with the average residence time of two minutes, a very high degree of the exchange reaction can be obtained. Using 0.2 percent of TsOH we obtained 5 to 23 percent conversion, depending on the temperature. It is easy to calculate that if one ester-amide reaction occurs per macromolecule, the conversion should be about 1 percent. The results obtained simply demonstrated a great potential for achieving a controlled exchange reaction. The conditions will have to be optimized. Usually addition of about 10 percent of a block polymer is sufficient to secure compatibility in most polymer blends. This means that probably 0.1 to 0.7 percent conversion will be sufficient to secure good mechanical properties, *i.e.* we have plenty of room to maneuver in order to accomplish our task. The key to success will be the kinetic study of the relative reaction rates for the exchange and for the degradation processes.

A Review of Miscibility Enhancement via Ion-Dipole Interactions*

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It is shown that ion-dipole interactions induce considerable miscibility enhancement in blends of styrene ionomers with poly(alkylene oxides). Dynamic mechanical studies, in conjunction with transparency and brittleness of the samples, are used to evaluate miscibility. The effect is clearly thermodynamic, in that phase separation can be induced in miscible samples by raising the temperature, with miscibility reestablished on cooling. The miscibility enhancement in these systems is compared with that resulting from hydrogen bonding. In addition to the styrene/alkylene oxide system, ion-dipole interactions are found to be effective in enhancing the miscibility of many ionic polymer/polar polymer pairs. The ionomers used in this study were styrene lithium methacrylate and ethyl acrylate lithium acrylate copolymers, while polyethers, polysulfides, polyesters, polyimines, and substituted polyethylenes served as polar polymers.

INTRODUCTION

It is well known that for thermodynamic reasons the majority of polymer pairs are not miscible. To achieve miscibility, the presence of specific attractive interactions is frequently required. The interactions studied to date include, among others, hydrogen bonding, donor-acceptor interactions, and dipole-dipole interactions (1 to 3). The properties of ionomers have been studied for many years in this laboratory. Recently, in the course of these studies, miscibility enhancement via polycation-polyanion interactions has been explored (4 to 6). While polystyrene (PS) and poly(ethyl acrylate) (PEA) or polystyrene and polyisoprene (PIP) are immiscible, miscibility was achieved by introducing, for example, small percentages of sulfonic acid groups into PS and of vinyl pyridine groups into PEA.

In this review, the enhancement of miscibility via ion-dipole interaction between ionomers and polar polymers is described (7 to 9). Ion-dipole interactions play an important role in such phenomena as dissolution of ionic compounds in highly polar solvents (e.g. NaCl in water) (10). In these cases, the free energy required to disrupt the strong attraction between solute particles is supplied mainly by the ion-dipole interaction between the

solute particles and the solvent molecules. Ion-dipole interactions between polar polymer and small ions have been investigated in the past. Moacanin and Cuddihy (11) and other groups (12, 13) found that poly(propylene oxide) interacts with LiClO_4 , leading to a dramatic increase in the viscosity and glass-transition temperature, which can be explained by the presence of strong interactions between the polymer and the ions. Thus, while ion-dipole interactions in small molecule-small molecule and polymer-small molecule systems are well known, as mentioned above, their role in miscibility enhancement in polymer-polymer systems has not, as yet, been explored, although numerous patents exist utilizing this interaction (14, 15).

In the first study of ion-dipole interactions as miscibility enhancers, a 9.5-mole percent lithium methacrylate copolymer in styrene, the ionic polymer, was mixed with various amounts of poly(alkylene oxides), i.e. poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPrO), the polar polymers. The effect of ion-dipole interactions was compared with that of hydrogen bonding in the styrene methacrylic acid system. Subsequently, the molecular-weight effect was studied using a high molecular weight ($M > 10^5$) and low molecular weight ($M < 10^4$) poly(alkylene oxide). The effect of ion content on miscibility enhancement by using 2, 6, 9,

* Presented in part at ACS meeting, St. Louis (April 1984) and reported in *Macromolecules*.

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and 16 percent ionomers at a constant PEO content was also explored.

In order to show the general applicability of ion-dipole interactions as miscibility enhancers in ionomer/polar polymer systems, several additional pairs were explored covering a wide range of polar polymers. A styrene lithium methacrylate copolymer and an ethyl acrylate lithium acrylate copolymer were used as the ionomers, while polyethers, polyesters, a polysulfide, a polyimine, and substituted polyethylenes were used as the polar polymers.

A very wide range of experimental techniques have been used to evaluate miscibility in polymers (1 to 3). In this work, three were utilized. The first and most extensively used method involves the study of dynamic mechanical properties utilizing a torsion pendulum at an approximate frequency of 1 Hz. These studies were supplemented by checking the transparency and brittleness of the samples. Transparency is a very sensitive method for detection of heterogeneity in polymers. It has been shown, for example, that only 0.01 percent of poly(methyl methacrylate) in polystyrene leads to the presence of cloudiness (16), a characteristic feature of immiscible materials in which the refractive index difference is 0.1 or greater, which is the case in the PS-PPrO system. Brittleness in blends is usually indicative of poor mixing, and was utilized here also, although only on a very qualitative basis.

Finally, the transmitted light intensity was measured for styrene ionomer/poly(alkylene oxide) systems in order to study the phase-separation behavior as a function of temperature. It has been recognized that LCST behavior is rather common for some miscible blend systems (17, 18, 24). Phase separation normally takes place at the cloud point in these systems on raising the temperature. In this work it was shown that the styrene ionomer/poly(alkylene oxide) system is subject to this type of behavior, and the effect of ion content on the cloud point curve was examined.

EXPERIMENTAL

Materials

The styrene-methacrylic acid and ethyl acrylate-acrylic acid copolymers were synthesized in connection with other projects by procedures described elsewhere (19, 20). The neutralizations were carried out by adding predetermined amounts of methanolic LiOH to the polymer solutions. High-molecular-weight poly(propylene oxide) was provided by Dr. E. J. Vandenberg, and other polar polymers were purchased from Polysciences and Aldrich. Molecular weights for poly(alkylene oxide) systems are shown in Table 1.

Blending

The ionomer and polar polymer were separately dissolved in an appropriate common solvent at concentrations of ca. 1 wt percent. The polar polymer solution was then added to the ionomer solution slowly with stirring. All the solutions were clear.

Table 1. Molecular Weights of Polymers for Poly(alkylene oxide) Systems (after Ref. 7).

Polymer	Symbol	Molecular Weight
Polystyrene	PS	$(1.25-2.5) \times 10^5$
PS ionomer with 9.5 mol % MAA	S-0.095MAA-Li	1×10^5
Poly(ethylene oxide)	PEO(h)*	4×10^5
Poly(ethylene glycol)	PEO(l)*	3.4×10^3
Poly(propylene oxide)		
elastomer	PPrO(h)	6×10^5
liquid	PPrO(l)	4×10^3

* (h) refers to high molecular weight $>10^5$

(l) refers to low molecular weight $<10^3$

Solid polymer blends were obtained by three different methods depending on the solvent: freeze-drying, precipitation into a common nonsolvent, or evaporation. After drying under vacuum at a high temperature (80°C) for 1 to 7 days, the polymers were compression molded under an applied load of 4000 lbs/in² at temperatures slightly higher than T_g . Typical dimensions of the rectangular specimens for torsion pendulum measurements were 3.0 by 6.0 by 50 mm. The disk samples for transparency measurements were also compression molded, typical dimensions being radius = 6.5 mm and thickness = 0.5 mm.

Measurements

Dynamic mechanical studies of the blend samples were performed using a computerized torsion pendulum, an early version of which is described elsewhere (21). The frequencies varied from ca. 3 Hz for the glassy region to ca. 0.1 Hz for the low-modulus region. The heating rate was usually 0.6°C/min with a temperature control of $\pm 1^\circ\text{C}$.

The thermal analyses for styrene/poly(alkylene oxide) systems were performed using a Perkin-Elmer differential-scanning calorimeter (Model DSC-2).

To observe the phase-separation behavior, a disk sample was mounted on a 1-mm-thick microscope slide glass and covered with a 0.20-mm-thick cover glass. The assembly was then placed on an FP52 hot stage mounted on the microscope. The heating rate was 1 to 2 deg/min regulated by a Mettler FP5. Transmitted light intensity was recorded as an output voltage on a recorder using a photocell at the eyepiece position.

RESULTS AND DISCUSSION

Poly(alkylene oxide) Systems

In the complete absence of ionic groups, PS and PEO are shown to be immiscible. This can be seen quite clearly on examining a plot of the storage modulus, G' and the loss modulus, G'' as a function of temperature for blends of PS and PEO (not shown). The drop in the G' , indicative of the glass-transition temperature, occurs for all materials over the whole range of PS/PEO contents at approximately the same temperature, indicating the absence of interactions. It is also noteworthy that in this system the samples containing both PS and PEO

are quite opaque, and that the crystalline melting point, as determined by differential-scanning calorimetry, does not change as a function of sample composition. The samples are also quite brittle.

The behavior of PEO in the presence of PS ionomers is completely different. In these systems, ion-dipole interactions play a major role, as can be seen in a dramatic lowering of the primary glass-transition temperature with increasing PEO content. This is shown in Fig. 1 for G' and G'' as a function of a temperature. The lowering of the glass-transition temperature reflects a dramatic enhancement in miscibility in the presence of ionic groups. Furthermore, the 10 percent blend, as well as the pure PS ionomer, are completely clear. Some cloudiness is observed for the 20 percent sample, and the cloudiness increases progressively with increasing PEO content. DSC data show absolutely no crystallinity for the 10 and 20 percent blends; for the higher PEO contents, considerably less crystallinity is seen than in the corresponding non ionic PS/PEO systems.

It is also noteworthy that the high-temperature modulus, for example at 160°C, which in pure PS ionomers is indicative of the existence of ionic aggregates (22, 23), decreases with increasing PEO content. In Fig. 1, it drops by more than 1 order of magnitude on going from the pure PS ionomer to the 50 percent blend. It can be seen that as the PEO content decreases, the peak height of this low-

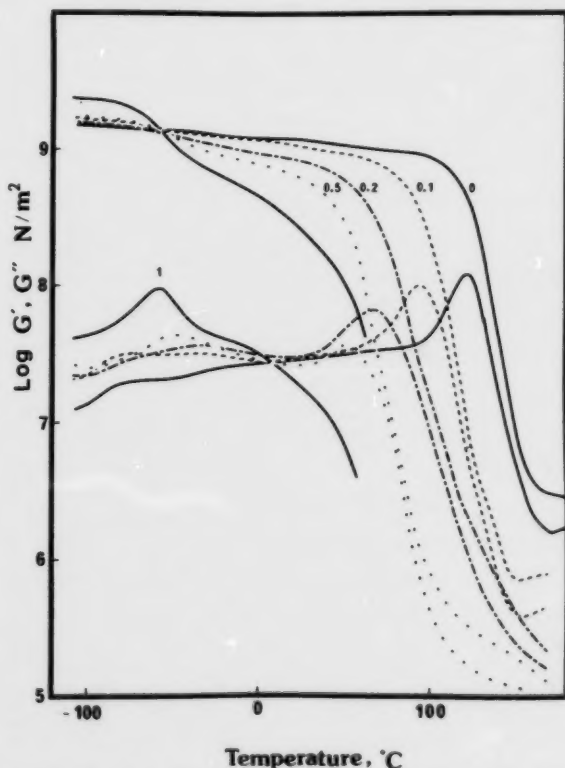


Fig. 1. Variation of the shear storage modulus, G' and the shear loss modulus, G'' with temperature for Blend S-0.095MAA-Li/PEO(h) of various PEO weight fractions. (after Ref. 7)

temperature peak decreases as well and moves to slightly higher temperatures.

The same phenomena were observed for the PPrO system. Both dynamic mechanical and DSC data show that PS and PPrO are immiscible in all composition ranges. By contrast, in the presence of the ionic groups, considerable miscibility enhancement is observed, although the PEO systems are more miscible with PS ionomers at comparable loading and ion content levels than the PPrO systems.

Comparison with Carboxylic Acid Systems

In order to compare the miscibility enhancement resulting from ion-dipole interactions with that resulting from the presence of a carboxylic acid in the same system, blends of PEO with the styrene-methacrylic acid copolymers were studied. Trends in behavior of $\log G'$ and $\log G''$ versus temperature are quite similar for the acid as for the ionomer. It is seen very clearly that, as in the ionomer case, the glass transition of the PS copolymer is depressed dramatically. Unlike the ionomer situation, however, the high-temperature-modulus (specifically the inflection point) characteristic of entanglements of ionic interactions occurs in this system at ca. 2×10^5 N/m², reflecting the absence of ionic interactions. It is also noteworthy that the steepness of the G' curve in the glass-transition region is much greater in the acid case than it was in the ionomer system in G' plots.

Molecular Weight Effects

It is generally recognized that a decrease of the molecular weight leads to considerable miscibility enhancement in polymer blends (1, 2, 24). To explore this effect in the present system, blends of both PEO and PPrO of low molecular weight were investigated here also. The storage and loss moduli as a function of temperature showed that the low-molecular-weight PEO or PPrO exhibited the same general trends as the high-molecular-weight samples. The glass-transition temperature of the PS ionomer is depressed considerably with increasing PEO or PPrO content. Here, however, the depression of the glass-transition temperature is considerably higher than in the high-molecular-weight case. Sample transparency is also very much better in this system. Thus, the 20 percent sample is still transparent, and only the 30 percent sample begins to show the first indication of cloudiness.

Table 2. Effect of Ion Content on the G'' Peak Positions in the S-xMAA/PEO (Acid and Salt) Systems at $w = 0.5$ (after Ref. 7).

Ion Content x %	Salt			Acid		
	High T_g Peak °C	T_m Peak °C	Low T_g Peak °C	High T_g Peak °C	T_m Peak °C	Low T_g Peak °C
0	99	64	-56	99	64	-56
2.3	90	64	-47	96	65	-44
6.6	67	—	-44	48	—	-31
9.5	53	—	-49	40	—	-42
16.7	44	—	-42	—	—	—

Ion Content Effect

Table 2 shows the effect of ion content on miscibility in the mixtures of styrene methacrylic acid copolymers (acid and salt) with PEO. It is seen that the high T_g peak decreases with increasing ion content, while the low T_g peak increases slightly with increasing ion content. Table 2 also confirms that, for all practical purposes, ion-dipole interactions in this system are as effective as acid-dipole

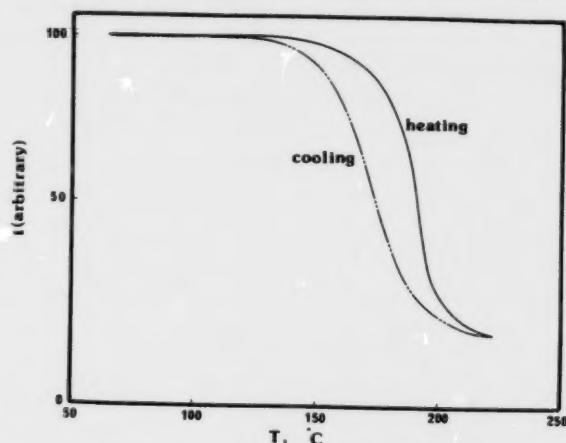


Fig. 2. Transparency measurement for Blend S-0.104MAA-Li/PPrO(l) at 15 percent loading level. (after Ref. 9)

interactions (possibly hydrogen bonding) in enhancing the miscibility.

Sample Transparency

Finally, in order to show that the miscibility enhancement is clearly thermodynamic, the measurement of the transmitted light was carried out. Figure 2 shows an example of the temperature dependence of transmitted light of a disk sample. The transmitted light intensity, I , starts to decrease at 136°C on heating and continues decreasing gradually until it levels off at about 220°C. Here, the sample is completely opaque. Upon cooling, I shows normal hysteresis in that the shape of the I versus T curve is quite similar but displaced somewhat along the T axis. The disk becomes transparent again. This figure shows that the phase-separation process for this sample is reversible and thus thermodynamic. Therefore, a phase diagram is obtained by this method. Preliminary data (9) show that increasing the ion-content shifts the cloud point curve to higher temperatures, as is expected from Table 2.

Other Systems

Table 3 shows the polymers and solvents used in the studies of miscibility in the other systems. The methods of preparing the blend, as well as the evaluation of miscibility are also shown. In the

Table 3. Summary of the Data for Ionomer/Polar Polymer Blends (after Ref. 8).

Ionomer	Polar Polymer	Chain Structure	Solvent	Preparative Method	Peak Shift	
					Pure Polymer	Ionomer
S-0.066MAA-Li	PVAc	$\begin{array}{c} \text{O} \\ \\ \text{C=O} \\ \\ \text{CH}_3 \end{array}$	Ben/MeOH(90/10)	freeze-drying	X	X
S-0.066MAA-Li	PDMS	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{Si-O} \\ \\ \text{CH}_3 \end{array}$	Ben/MeOH(90/10)	freeze-drying	X	X
S-0.066MAA-Li	PCL	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C-O} \\ \\ \text{O} \end{array}$	THF/MeOH(90/10)	precipitation	X	Δ
S-0.066MAA-Li	PVC	$\begin{array}{c} \text{O} \\ \\ \text{Cl} \end{array}$	THF/MeOH(90/10)	precipitation	X	O
EA-0.18AA-Li	PEI	$\begin{array}{c} \text{Cl} \\ \\ \text{N} \\ \\ \text{H} \end{array}$	DMF/H ₂ O(90/10)	evaporation	X	O
S-0.066MAA-Li	PET	$\begin{array}{c} \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \\ \quad \quad \quad \\ \text{O} \quad \quad \quad \text{O} \end{array}$	m-cresol/MeOH (90/10)	evaporation	X	Δ
S-0.066MAA-Li	PECH	$\begin{array}{c} \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \\ \quad \quad \quad \\ \text{O} \quad \quad \quad \text{O} \end{array}$	Ben/MeOH(90/10)	freeze-drying	X	Δ
S-0.066MAA-Li	PES	$\begin{array}{c} \text{CH}_2 \\ \\ \text{Cl} \\ \\ \text{C-O} \\ \\ \text{O} \end{array}$	THF/MeOH(90/10)	precipitation	X	Δ
S-0.066MAA-Li	PSu	$\begin{array}{c} \text{O} \\ \\ \text{S} \end{array}$	Ben/MeOH(90/10)	freeze-drying	X	Δ

X: no shift of peaks
 Δ : shift of peaks
 O: single peak

absence of ions, none of the pure polymer pairs are miscible. This was either confirmed in this laboratory or reported in the literature. All samples are opaque and many of them are brittle. However, the presence of small percentages of ions leads to an increase in miscibility, just as in the case of the PS ionomer/poly(alkylene oxide) systems. Most of the ionomer blends show at least a shift of the glass-transition temperature with increasing polar polymer content. Figure 3 shows the dynamic mechanical data for EA-0.18AA-Li/PEI blend, which shows a single glass transition. Furthermore, this blend sample is quite transparent even at a 50 percent loading level, while PEA and PEI form a completely opaque sample without ions. As a general trend, the polar polymers with less bulky side chains are more miscible than those with more bulky side chains. For example, polar polymers like PEO, PEI, and PSu, which have no bulky side groups, show good miscibility enhancement, while PVAc and PDMS, which have bulky side groups, show no miscibility.

CONCLUSION

The study has demonstrated that the presence of ion-dipole interactions enhances the miscibility of otherwise immiscible polymers. This is a general trend. Miscible samples are transparent; some become opaque on heating and become transparent

again on cooling. These samples usually have good mechanical properties. The degree of miscibility enhancement due to ion-dipole interactions, which is comparable to that due to hydrogen bonding, increases with increasing ion content. The molecular-weight effect is exactly as expected; the lower the molecular weight, the greater the effect. The primary factor which determines the miscibility for ionomer/polar polymer pairs is the ion-dipole interaction. However, as a secondary factor, the bulkiness of side groups is important, since it might dampen the ion-dipole interaction by changing the average distance between the ion and the dipole.

ACKNOWLEDGMENTS

We thank Dr. E. J. Vandenberg of Hercules, Inc., for kindly supplying the PPRo elastomer sample and Miss Sylvie Gauthier for preparing of the styrene methacrylic acid copolymer sample in connection with another project. We also thank Miss D. Wollmann and Miss M. Jolicoeur for their assistance in preparing some of the polymer blend samples. Financial support from the US Army Research Office is also gratefully acknowledged.

NOMENCLATURE

PCL	= Poly(caprolactone)
PEA	= Poly(ethyl acrylate)
PECH	= Poly(epichlorohydrin)
PEI	= Poly(ethyleneimine)
PEO	= Poly(ethylene oxide)
PES	= Poly(ethylene succinate)
PET	= Poly(ethylene terephthalate)
PPRo	= Poly(propylene oxide)
PS	= Polystyrene
PSu	= Polysulfide
PVAc	= Poly(vinyl acetate)
PVC	= Poly(vinyl chloride)

REFERENCES

1. D. R. Paul and S. Newman, "Polymer Blends", Academic Press, New York (1978).
2. O. Olabisi, L. M. Robeson, and M. T. Shaw, "Polymer-Polymer Miscibility", Academic Press, New York (1979).
3. S. L. Cooper and G. M. Estes ed., "Multiphase Polymers", *Adv. Chem. Ser.*, 176, Am. Chem. Soc., Washington (1979).
4. A. Eisenberg, P. Smith, and Z. L. Zhou, *Polym. Eng. Sci.*, 22, 1117 (1982).
5. P. Smith and A. Eisenberg, *J. Polym. Sci., Polym. Lett. Ed.*, 21, 223 (1983).
6. Z. L. Zhou and A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.*, 21, 595 (1983).
7. M. Hara and A. Eisenberg, *Macromolecules*, 17, 1335 (1984).
8. M. Hara, D. Wollmann, and A. Eisenberg, *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 25, 280 (1984).
9. M. Hara and A. Eisenberg, to be submitted.
10. R. W. Gurney, "Ions in Solution", Dover Publication, Inc., New York (1962).
11. J. Moacanin and E. F. Cuddihy, *J. Polym. Sci., Part C*, 14, 313 (1966).
12. R. E. Wetton, D. B. James, and W. Whiting, *J. Polym. Sci., Polym. Lett. Ed.*, 14, 577 (1976).
13. A. Eisenberg, K. Ovans, and H. N. Yoon, *Adv. Chem. Ser.*, 187, 267 (1980).
14. E. F. Lopez, L. C. Glover, and B. J. Lyons, U.S. Pat. 4018733 (1977) (assigned to Raychem Corp.).
15. J. J. Dolce, U.S. Pat. 4002581 (1977) (assigned to General Electric Co.).

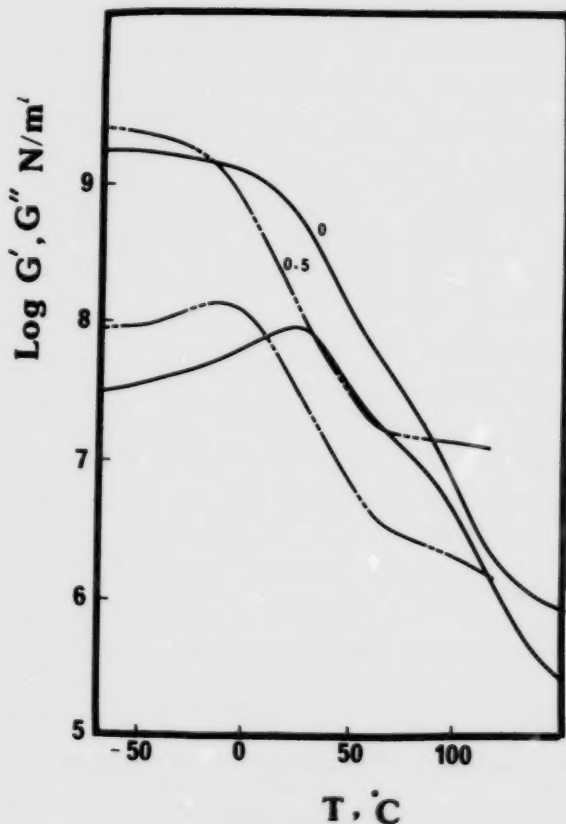


Fig. 3. Variation of the shear storage modulus, G' and the shear loss modulus, G'' with temperature for Blend EA-0.18AA-Li/PEI at 50 percent loading level.

16. H. K. Yuen and J. B. Kinsinger, *Macromolecules*, **7**, 329 (1974).
17. R. E. Bernstein, C. A. Cruz, D. R. Paul, and J. W. Barlow, *Macromolecules*, **10**, 681 (1977).
18. D. Patterson and A. Robard, *Macromolecules*, **11**, 690 (1978).
19. S. Gauthier and A. Eisenberg, to be published.
20. H. Matsuura and A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1201 (1976).
21. B. Cayrol, Ph. D. Thesis, McGill University, Montreal, 1978.
22. L. Holliday, "Ionic Polymers", Applied Science Publishers, London (1975).
23. A. Eisenberg and M. King, "Ion-Containing Polymers", Academic Press, New York (1977).
24. L. P. McMaster, *Macromolecules*, **6**, 760 (1973).
25. R. Buchdahl and L. E. Nielsen, *J. Polym. Sci.*, **15**, 1 (1955).
26. S. Manabe, R. Murakami, M. Takayanagi, and S. Uemura, *Int. J. Polym. Mater.*, **1**, 47 (1971).

DISCUSSION

R. Simha: Referring to your last table, Adi, have you attempted to obtain some correlation between the dipole strength and the compatibilizing effect? We have some information in the low-molecular-weight analogues. Can one make any rationalization of the hierarchy in your last table?

A. Eisenberg: What seems to be even more important than the dipole strength is the position of the dipole. For example, pendant ester groups do not really work well but those on the main chain do.

L. A. Utracki: Was the compatibilization partial?

A. Eisenberg: Yes, however, what is partial with 50 percent PEO may be total with 10 percent. For example, the styrene ionomer/PEO system at 10 percent is well within the miscible, transparent region, whereas at 50 percent it is already above the phase-separation line. The choice of the 50 to 50 concentration level was arbitrarily selected for experimental convenience. We know that if we see a peak shift at this concentration, we may be able to find complete miscibility at lower PEO content. I am sorry that due to the limited number of systems examined to date I cannot answer you more completely.

T. M. Malik: Do you think that one could get more insight using an electrical field? I believe that, for your polymers, at the glass-transition temperature, the peak in T_g is due to polar-group rotation. This is particularly true for PEO. If you do the electrical field measurements, you could calculate dipole moments, and correlation factors, and see in more detail what is happening upon addition of ions.

A. Eisenberg: Absolutely. We have a 1621 General Radio bridge and the cell is being made. We hope that dielectric studies will improve our understanding of the system.

C. Sadr: In the two incompatible systems you did not have any change of the peak position but the peak height decreased. What can the reason be for this?

A. Eisenberg: Conceivably the mass effect. If you have less material per unit volume, the intensity of the dispersion must decrease. There may also be other reasons.

L. A. Utracki: It seems that here there are two factors: the strength of ion-dipole interactions and the chain flexibility. If the molecules were rigid, it could not efficiently participate in the ion-dipole cluster. I presume that this may explain your beautiful results with the flexible-chain, PPO, PEI, or PEO. I would venture a guess that with these highly flexible macromolecules your compatibilization method work is beyond the thermodynamically predicted sharp decrease of miscibility with the increase of molecular weight.

A. Eisenberg: In the PEO and PPO, which are the only ones where we looked at both low- and high-molecular-weight samples, you are absolutely right—we did find excellent compatibility for the high molecular material also. In terms of chain flexibility, surely one cannot disagree with your statement. The molecular-weight effect is there in the sense that the very high molecular weights are somewhat less miscible than the low-molecular-weight material, but we have gone from a thousand to a million and found good miscibility in all cases.

R. E. Prud'homme: I would like to mention that in blends of polyesters with chlorinated polymers we always observed that one requirement for miscibility was the ratio of the number of methylene groups to the number of carbonyl groups in the repeat unit of these polymers. We observed that the low values of this ratio led to the immiscibility of the polymers. Following the observation made for linear polyesters with chlorinated polymers, we observed the same effect for aromatic polyesters with chlorinated polymers. A similar observation was reported by D. R. Paul for polycarbonate with polyesters. I would like to suggest that instead of PET you try poly(butylene terephthalate) or poly(hexamethylene terephthalate). These could show high miscibility with ionomers than PET.

A. Eisenberg: That is a very good idea. Thank you very much.

H. P. Schreiber: You concentrated on the solid-state properties. How persistent are these ion-dipole interactions in the melt? Could you comment on thermal and shear ability of these complexes.

A. Eisenberg: G. C. Baznin and I looked at the rheology of the ion-ion blends, but not the ion-dipole systems as yet. The ion-ion blends essentially show no change in the height of the rubbery plateau region—it stays right where it was for the nonionic system. What changes is what I would call the "apparent molecular weight". The ionic interactions persist, but basically their action is not cross-linking but rather a slowdown of the rate of disentanglement.

H. P. Schreiber: And this is both a function of temperature and shear field intensity.

A. Eisenberg: We have not looked at the shear dependence yet. So far, we looked only at the master curves for different ion contents. They looked exactly like a single polymer of progressively higher molecular weight.

Polycarbonate Blends with Polystyrene and Polypropylene

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Blends of polycarbonate/polystyrene (PC/PS), polycarbonate/polypropylene (PC/PP) and ternary blends of the three components (PC/PS/PP) were studied. Extrudate swell of the molten blends increased with increasing concentrations of the minor components and leveled off at characteristic blend compositions. These compositions corresponded to the limits of compatibility as judged by the onset of brittleness in tensile tests. Both PS and PP appear to have some limited practical compatibility with PC. The change in extrudate swell behavior with concentration may be a rapid and convenient test for the effective concentration limits of partially miscible polymers.

INTRODUCTION

When the overall balance of properties and costs of a polymeric material is not entirely satisfactory it can be adjusted either by modifying the polymer structure, as by copolymerization, or by blending with other materials. Blending does not always provide a satisfactory alternative to copolymerization, but it is the less expensive and therefore the preferred route when it is effective. Polymer blends are being used successfully in an increasing number of applications. The pace of development has been accelerated by the realization that the production of stable mixtures does not necessarily require the use of thermodynamically stable systems (1).

This research involved the study of blends of polycarbonate/polystyrene (PC/PS), polycarbonate/polypropylene (PC/PP), and ternary blends of the three components (PC/PS/PP).

Polystyrene-polycarbonate blends are well-known articles of commerce and are used primarily to improve the cost/performance ratio of the more expensive polycarbonate. Blends of polycarbonate with polypropylene are reported to provide a lower melt viscosity (2) and better impact strength (3). It has been suggested that the two polymers are miscible at low polypropylene concentrations (4).

PP and PS are both believed to have limited compatibility with PC. A major aim of this research was to determine whether miscibility limits could be determined by melt rheology measurements that are relatively fast and simple.

EXPERIMENTAL

The polycarbonate was a bis phenol-A based molding material. Two styrene homopolymers were studied. Molecular weights of these materials are listed in Table 1. Molecular-weight characterization

was by gel permeation chromatography in tetrahydrofuran solutions with cross-linked polystyrene gel column packings, at 23°C. The universal calibration method was based on hydrodynamic volumes (5, 6). The polypropylene was a 3.0-melt-flow homopolymer, with density 0.905 g/mL.

All mixtures were dried in a vacuum oven at 80°C for 48 hours. Granule blends were mixed and then extruded through a one-half-inch screw extruder, with a 27 to 1 length-to-diameter screw. A metering screw with 3 to 1 compression ratio was used. Table 2 lists the extrusion conditions during blending. Temperatures were approximately constant for each material, regardless of screw speed. The extrusion temperature was deliberately chosen to be cool for polycarbonate, to limit degradation of the polystyrene and polypropylene.

To minimize hydrolysis, the extruder hopper was connected to a desiccating dryer that pumped warm, dry air through the granules. Melt flow properties were measured using the screw extruder. Operating conditions were the same as those used during blending. Raw data were obtained by cutting and weighing the extrudates obtained at various screw speeds and die head pressures. Mass flow rates were converted to volumetric flow rates by dividing by the melt densities reported for polycarbonate (7), polypropylene (8), and polystyrene (9). The melt densities of the mixture were calculated from:

$$\rho_m = \left[\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \right]^{-1} \quad (1)$$

for binary blends, and

$$\rho_m = \left[\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} + \frac{w_3}{\rho_3} \right]^{-1} \quad (2)$$

for ternary blends,

Table 1. Molecular Weights of Polycarbonate and Polystyrenes.

Homopolymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$
Polystyrene A	79,000	220,000	445,000
Polystyrene B	58,000	256,000	534,000
Polycarbonate	15,300	31,500	53,000

Table 2. Extrusion Conditions during Blending.

Polymer	Temperature ^a Setting, °C	Die Face ^b Temperature, °C	Extrudate ^b Temperature, °C
PC	250	216	257
PS	250	208	249
PP	250	208	246
PC/PS blends	250	214	256
PC/PP blends	250	212	256
PC/PP/PS blends	250	212	252

^a All temperatures (barrel zones, die-head, die) were the same.

^b Measured with a needle pyrometer.

where ρ and w denote densities and weight fractions, respectively, and the suffixes m , 1, 2, and 3 refer to the mixture and to the various homopolymers in the mixtures.

Order of magnitude values for melt compressibility (10) are very low and the errors involved in assuming that the polymer melt density was independent of pressure were considered to be negligible.

Flat-entry capillary dies of known dimensions were used and apparent shear-stress and apparent shear-rate values were calculated from these dimensions and the corresponding pressure drops or mass flow rates, respectively.

Extrudate swell was measured on frozen, unannealed extrudates and is reported as:

% Extrudate Swell

$$= \frac{D(\text{ext}) - D(\text{die})}{D(\text{die})} \times 100\% \quad (3)$$

where $D(\text{die})$ and $D(\text{ext})$ refer to the diameters of the die capillary and extrudate, respectively.

The densities of solid homopolymers and blends were determined at room temperature using the pycnometer method of ASTM D 792 (11). Results of density measurements on homopolymers were consistent with literature values, as shown in Table 3. Tensile tests were performed using an Instron Tester. Sample specifications and testing methods conformed to ASTM D 1708 at a crosshead speed of 1.0 cm/minute. The test specimens were made by compression molding of the homopolymers and polyblends, after predrying as described above. Samples were compression molded at 270°C.

RESULTS

Densities

Results of density measurements are compared with calculated values in Figs. 1 to 3. There is no significant deviation between measured and calcu-

lated densities in PC/PS blends up to 25 percent PS contents. Blends containing 25 and 30 percent PS were denser than expected, however. Densities measured in PC/PP blends were all lower than calculated, with the difference increasing with increasing PP content (Fig. 2). The density difference was 6 percent at 15 weight percent PP, increasing to 8 percent at 0.15 weight fraction PP.

The ternary blends studied all contained 5 percent PP and varying PS levels up to 30 percent. Figure 3 shows that the measured values were about

Table 3. Densities of Homopolymers—Measured and Literature Values.

Species	Densities g/cm ³	
	Measured	Literature
PC	1.202	1.200 (12)
PS	1.046	1.050 (13)
PP	0.907	0.905 (14)

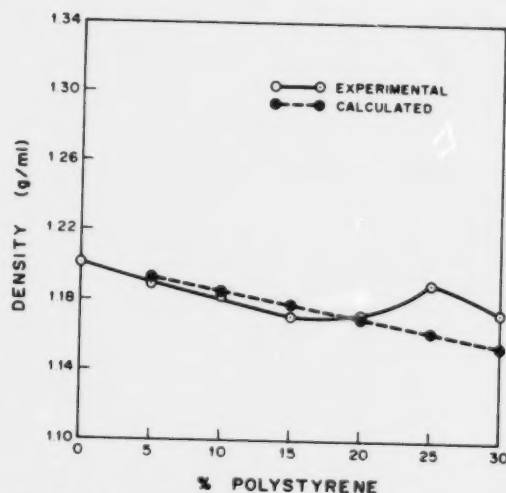


Fig. 1. Plot of density versus weight percent polystyrene in PC/PS blends; 23°C.

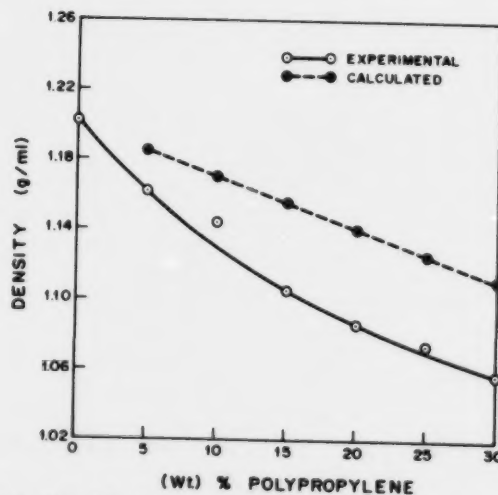


Fig. 2. Plot of density versus weight percent polypropylene in PC/PP blends; 23°C.

0.03 g/mL lower than the expected figures. A blend containing 5 percent PP and 10 percent PS would thus produce articles with about 5 percent more volume than from the polycarbonate itself.

Melt Flow

Mass-flow rate screw-speed relations were linear at all screw speeds, for the materials studied. At a given speed, the relative rates of extrusion, on a weight/time basis are: polystyrene > polycarbonate > polypropylene. This is seen, for example, in Fig. 4. The order probably arises because the melt density of PP is lower than that of the other two polymers, while PS softens at lower temperatures than PC.

Volumetric flow rates are shown as functions of screw speed in Figs. 5 to 7. The extrusion rate of blends with polypropylene is not higher than that of polycarbonate itself, except perhaps at the highest screw speeds. Inclusion of PS does not enhance the extrusion rate of PC although the PS itself extrudes faster than either of the other two polymers at this temperature.

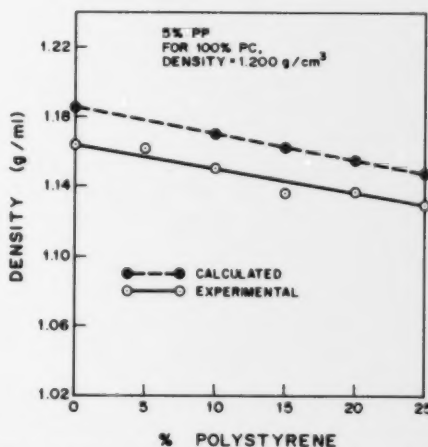


Fig. 3. Plot of density versus weight percent polystyrene in PC/PP/PS ternary blends containing 5 percent polypropylene; 23 °C.

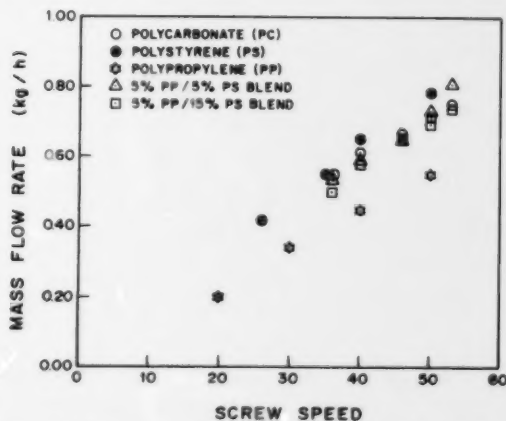


Fig. 4. Mass-flow rate (kg/h) versus screw speed (rpm) for PC/PS/PP ternary blends; 250 °C; die L/D = 28.4.

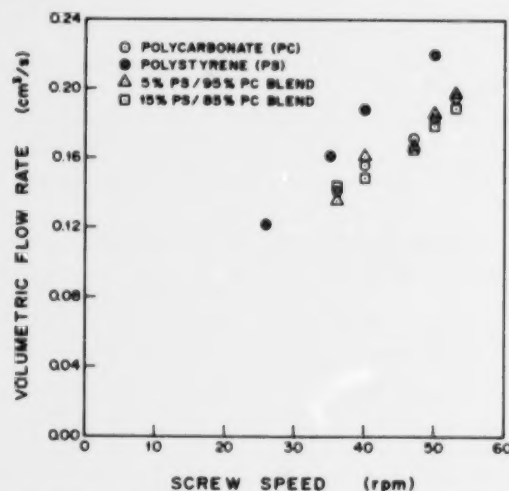


Fig. 5. Volumetric flow rate (cm³/s) versus screw speed (rpm) for PC/PS blends; 250 °C; die L/D = 28.4.

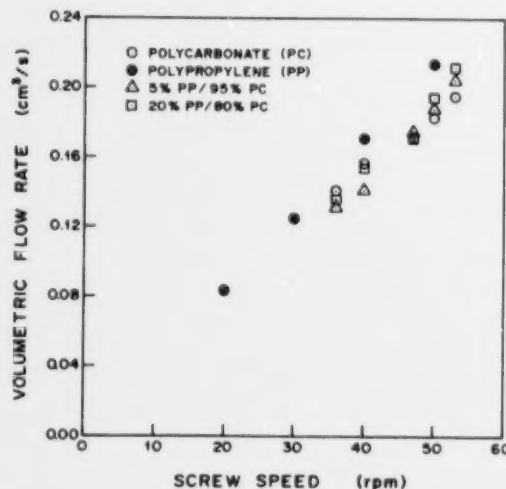


Fig. 6. Volumetric flow rate (cm³/s) versus screw speed (rpm) for PC/PP blends; 250 °C; die L/D = 28.4.

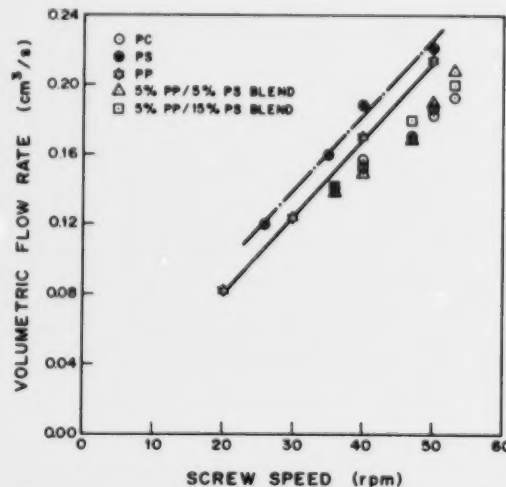


Fig. 7. Volumetric flow rate (cm³/s) versus screw speed (rpm) for PC/PP/PS ternary blends; 250 °C; die L/D = 28.4.

Figures 8 to 10 show apparent flow curves at a common melt temperature in a single flat-entry capillary orifice. All shear stress-shear rate relations for blends are intermediate between those of the components. Blending with PP does provide a lower melt viscosity, as has been reported by others (2). It is not an effective processing aid for PC in these experiments, however, because it does not enhance the extrusion rate at given screw speed. Output rates in larger screw extruders are limited primarily by the rates at which polymer granules are softened in the machine (10). It that case, we would expect that both PP and PS would function as processing aids, since heat will be conducted more readily through a bed of PC pellets that contains softened

regions of the other polymers. The apparent flow curves of Figs. 8 to 10 also suggest that the extruder power requirements will be lower for blends than for PC alone.

Extrudate Swell

Figures 11 to 13 are plots of extrudate swell versus blend composition, at a fixed screw rpm at 250°C. It is interesting to note that all figures show a general increase in extrudate swell followed by a levelling off at some blend composition. It may be postulated that the change in slope of the die swell-composition curve may indicate the limit of compatibility of the minor component in the matrix polymer. It is known that small concentrations of a partially miscible second polymer may be used to reduce elastic melt properties, like die swell (15).

For PC/PS and PC/PP blends the maximum level of extrudate swell is reached at 15 weight percent

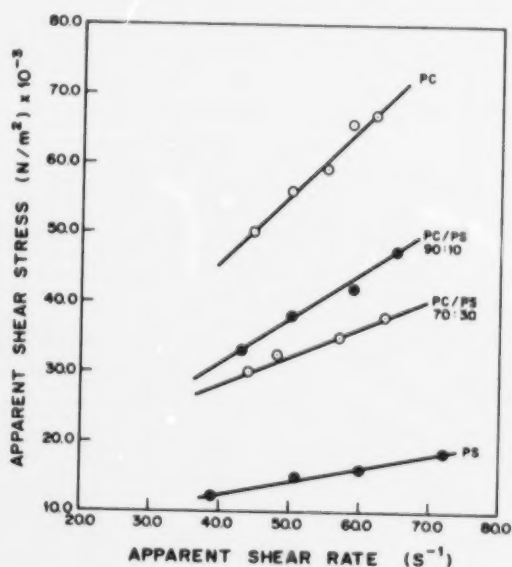


Fig. 8. Apparent flow curves for PS/PC blends; 250°C; capillary die with $L/D = 28.4$.

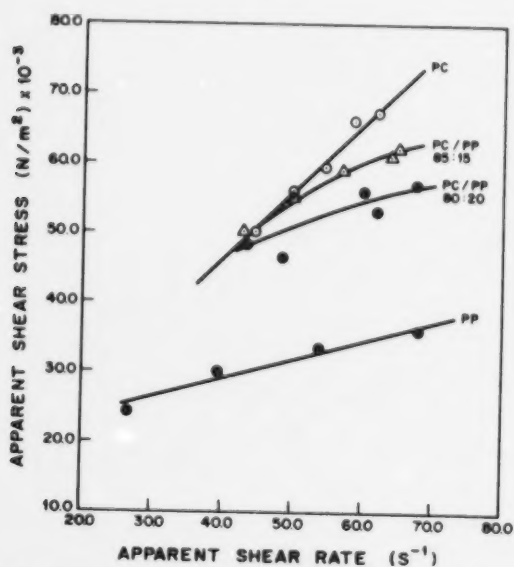


Fig. 9. Apparent shear stress versus apparent shear rate for PC/PP blends; 250°C; $L/D = 28.4$ die.

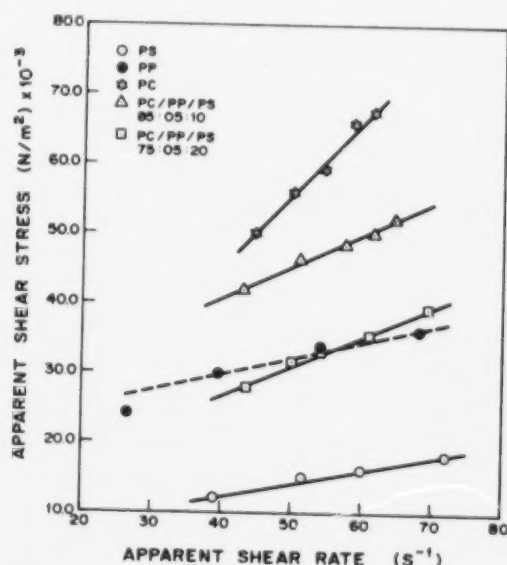


Fig. 10. Apparent flow curves for PS/PC/PP blends; 250°C, $L/D = 28.4$ die.

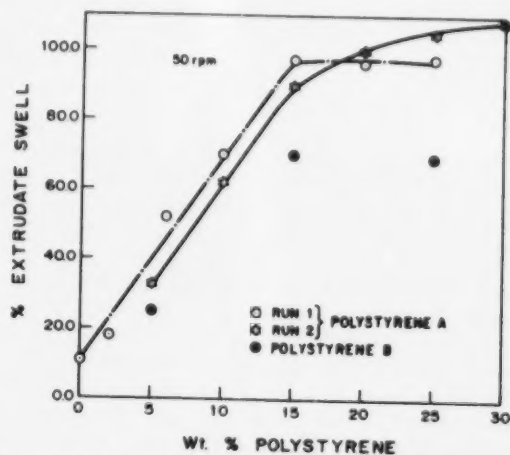


Fig. 11. Plot of extrudate swell versus percent PS in PC/PS blends; $L/D = 28.4$ die; 250°C.

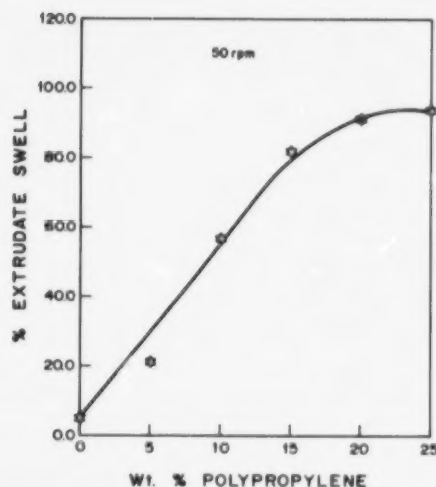


Fig. 12. Extrudate swell versus percent PP in PC/PP blends; $L/D = 28.4$ die; 250°C .

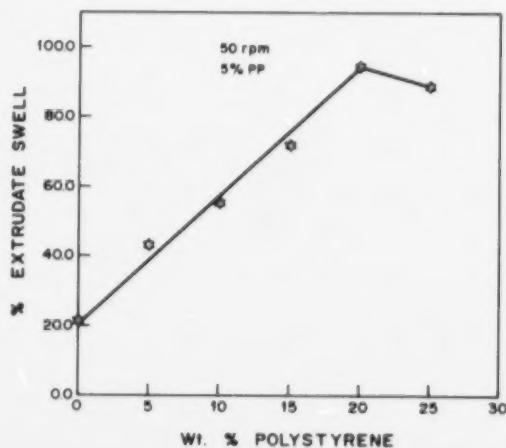


Fig. 13. Extrudate swell versus percent PS in PC/PP/PS ternary blends containing 5 percent PP; $L/D = 28.4$ die; 250°C .

of the minor component in PC. For PC/PS/PP blends containing 5 percent PP this occurs at 20 percent loading of PS. This behavior is compared to stress-strain characteristics in the following paragraphs.

Tensile Tests

Sharp yielding was observed in tensile testing of 100 percent PC and for PC/PS blends with less than 20 percent PS. The yield point was not as sharp for PC/PS/PP ternary blends, with 5 percent PP and up to 20 percent PS. The yield point was even broader for PC/PP alloys than for the ternary blends. At 20 percent PP, for example, the yield peak was broadened to the extent that there was almost a flat plateau in the load-elongation plot.

Figure 14 is a plot of yield and breaking (ultimate) strengths for PC/PS blends. Breaking strength decreases slightly up to about 20 weight percent PS, followed by a more rapid decrease with increasing PS content. The yield strength was equal to that of

polycarbonate, for blends that yielded in tension (i.e. with PS ≤ 15 weight percent).

Elongations at yield and at break are plotted against PS content in Fig. 15. The yield elongation was equal to that of PC alone for blends with up to 15 percent PS. Alloys with higher PS content did not exhibit clearly defined yield points and generally broke in a more brittle manner (i.e. with decreased elongation at break). It is interesting that the onset of brittle behaviour in solid alloys corresponds to about the same composition that exhibited a change in melt elastic behaviour (cf. Figs. 11 and 15).

The modulus of PC/PP blends decreased continuously with increasing PP content. Breaking strength and yield strength also showed a general decrease as the PP content was augmented. At 10 weight percent PP, for example, the ultimate

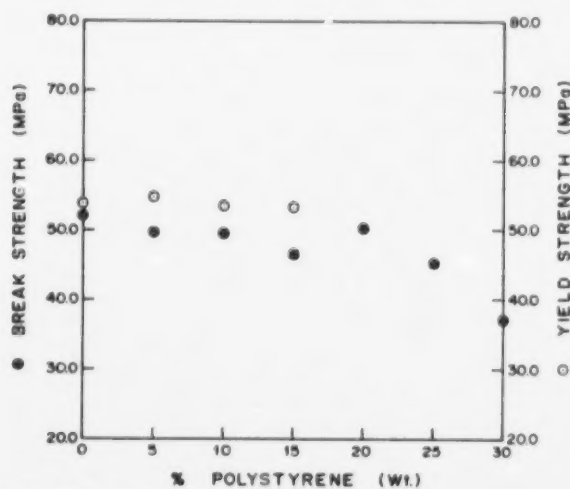


Fig. 14. Plot of breaking and yield stresses versus composition in PS/PC blends (polystyrene B).

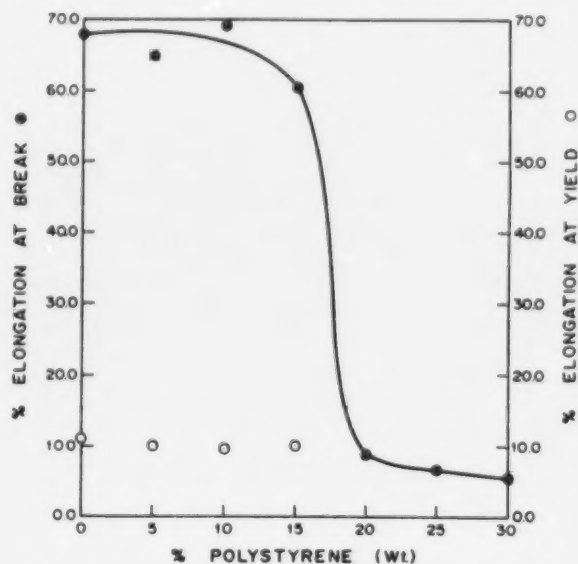


Fig. 15. Elongations at yield and break versus composition in PC/PS blends (with polystyrene B).

strength of the blend was 14 percent less than that of PC alone.

Figure 16 is a plot of elongations at yield and break versus composition, for PC/PP mixtures. The yield elongation is constant up to 20 percent PP, but the elongation at break decreases for PP concentrations ≥ 10 percent. The corresponding die-swell values leveled off at about 15 to 20 percent PP (Fig. 12).

The ternary PC/PP/PS blends examined all contained 5 weight percent PP. Comparison of these blends with PC/PS alloys shows a delay in the onset of brittle fracture with increasing PS content. Thus, ternary blends with 20 percent PS yielded, whereas binary blends showed no yield in slow tensile-elongation tests if the PS content was greater than 15 percent. Figure 17 shows a consistent decrease in elongation at break with increasing PS content. The elongation at yield remains constant up to 20 percent PS. This is the composition which the extrudate swell also changed (Fig. 13).

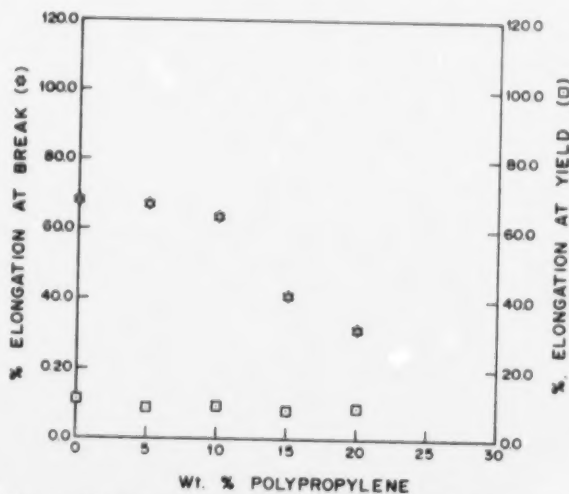


Fig. 16. Elongations at yield and break versus weight percent PP in PC/PP blends.

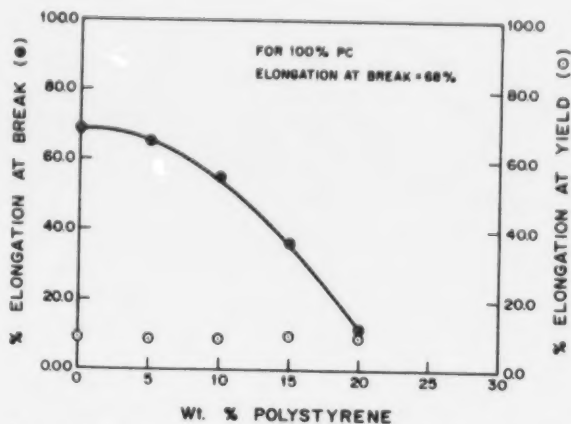


Fig. 17. Elongations at yield and break versus weight percent PS in PC/PS/PP blends containing 5 weight percent PP.

DISCUSSION

All PC/PS blends were transparent solids. Although the homopolymers are not considered to be miscible (16) their refractive indices are comparatively close (1.587 for PC and 1.590 for PS) and this may account for the good optical properties of their blends. All blends containing PP were white and opaque.

The results reported here indicate that PS and PP both may have some limited practical compatibility with PC. Useful products can be made within these limits, which are at about 15 percent PS and 5 percent PP, for the materials studied here. Blends with PP had lower densities than expected from the properties of the components alone, thus providing a volume/weight advantage. An offsetting disadvantage is the loss in transparency with the inclusion of PP in PC blends.

Extrudate swell of the molten blends increased in this case with increasing concentration of minor components and leveled off at characteristic blend positions. These compositions corresponded to the limits of compatibility as judged by the onset of brittleness in tensile tests of solid samples. Although this behavior can be rationalized, it is not known whether it is a general phenomenon. If it is, die swell measurements will be a convenient and rapid method for determining the effective concentration limits for blends of partially miscible polymers.

ACKNOWLEDGMENT

This research was supported by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

1. A. Rudin, *J. Macromol. Sci.-Revs. Macromol. Chem.*, C19, 267 (1980).
2. V. Dobrescu and V. Cobzaru, *J. Polym. Sci. Polym. Symp.*, 64, 27 (1978).
3. Japanese Pat. 14 581 (1966).
4. Z. Dobkowski, Z. Kohman, and B. Krajewski, in "Polymer Blends," E. Martuscelli, R. Palumbo, and M. Kryszewski, eds., Plenum Press, New York, (1980).
5. A. Rudin and R. A. Wagner, *J. Appl. Polym. Sci.*, 20, 1483 (1976).
6. H. K. Mahabadi and A. Rudin, *Polymer J.*, 4, 123 (1979).
7. Z. Dobkowski, *Polimery (Warsaw)*, 25, 110 (1978).
8. A. Rudin, K. K. Chee, and J. H. Shaw, *J. Polym. Sci., C*, 30, 415 (1970).
9. K. K. Chee and A. Rudin, *J. Macromol. Sci.-Phys.*, B7, 503 (1973).
10. Z. Tadmor and C. G. Gogos, "Principles of Polymer Processing," Wiley, New York, (1979).
11. American Society for Testing Materials, Philadelphia, PA., (1983).
12. D. W. Fox, "Polycarbonates," *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York, 3rd edition, Vol. 18, p. 479 (1982).
13. L. A. Utracki, *Polym. Eng. Sci.*, 22, 1166 (1982).
14. Shell Chemicals monograph, "Polypropylene."
15. A. Rudin and H. P. Schreiber, *Polym. Eng. Sci.*, 23, 422 (1983).
16. S. Krause, *J. Macromol. Sci.-Revs. Macromol. Chem.*, C7, 251 (1972).

DISCUSSION

M. R. Kamal: You showed the extrusion results which did not agree with your rheological findings

that there was a significant decrease of the viscosity at a given shear stress or shear rate. I wonder if you plotted your extrusion results as a function of the pressure drop, ΔP , rather than function of RPM you would not avoid this apparent inconsistency.

A. Rudin: I think that you are right. We simply used this plot as a more commonly used form. People think that if you added more processing aid you should get more output per RPM.

G. Vexler: Have you done any structural analysis for these mixtures?

A. Rudin: No.

Y. Ilahie: At the critical concentration of polymer, above which you did not see any increase in the extrudate swell, did you observe any surface roughness or melt fracture?

A. Rudin: In this particular case we did not have any melt fracture problem. In other systems it may be another story.

R. E. Prud'homme: I agree with a lot of things you said. However, I must confess that I disagree with your suggestion of using the solubility parameter, δ , to predict the miscibility of polymer blends. This parameter was derived for low-molecular-weight nonpolar systems. To apply this to polar polymers creates many problems. I can list at least a dozen miscible systems where the solubility parameters do not match, and another dozen immiscible systems where there is a close agreement of δ 's. I think that this concept should not be used to predict polymer/polymer miscibility.

A. Rudin: The reason I put it on the slide is that the solubility parameter is a very simple concept used by many. The only trouble is that it does not work reliably.

L. A. Utracki: Could you say a few words as to how the extrudate swell was measured? Are these curves independent of the extrusion rate? Are your conclusions independent of the extrusion parameters: e.g. screw speed, temperature, die configuration, method of up-take ...?

A. Rudin: These data were taken under one set of conditions. They are certainly not independent of die configuration and the strands were not annealed. These are not equilibrium data. They are reported as a function of composition for a given RPM. We did measure them at different screw speeds and determined their increase with the apparent shear rate in the die. As a general rule I think that the extrudate swell as a function of shear rate would not be independent of screw speed. However, in this particular case, because we have a low-molecular-weight material as a matrix, (polycarbonate with $M_n = 13,000$) I think that the screw-speed effect at a given shear rate would be small. In other cases, I would expect it to be significant. We have seen large effects in the high-molecular-weight LDPE where at the same $\dot{\gamma}$, the extrudate swell was very different depending on what screw we used.

L. A. Utracki: You are referring to the shear disentanglement. You are also familiar with the so-called shear compatibilization, widely used in the trade.

Obviously the method which you are suggesting, based on constancy of the extrudate swell, should be viewed with suspicion. It is, at best, a relative method of rating various pairs of polymers under rigidly controlled conditions. It may work in some cases but in general, it cannot be reliable.

A. Rudin: Why?

L. A. Utracki: For a number of reasons already mentioned during the discussion: dependence of extrudate swell on the extrusion condition, shear refining, shear compatibilization, shear fractionation, etc.,

A. Rudin: But is it not good for practical applications? If someone is going to extrude the blend, he is interested if the polymers are compatible under given conditions. I agree that the effects you mentioned are real and the method cannot be viewed as a thermodynamic tool to study the general miscibility of a pair of polymers. But it provides a quick answer about the compatibility of a specific extrudate. Is that not what we want?

L. A. Utracki: I believe that we need more; we have to know if that extrudate will be useful after a certain time. As you yourself wrote earlier, it is important to know if the blend will be stable during the required lifetime. Phase ripening for PVC blend siding would eliminate its usefulness. We need to know its miscibility, or to relax it, its compatibility near the equilibrium conditions. There are certain rheological methods which can provide this information. Later on M. Dumoulin will discuss a couple of rheological functions which can provide information regarding the apparent molecular weights of annealed blend samples, i.e. provide quantitative information on the degree of miscibility.

H. P. Schreiber: What Alfred was trying to say is that the method is reliable as long as the polymer-relaxation time is short so that it is the shear rate in the die which determines the post-extrusion swelling. For the higher molecular weights Leszek and the company are perfectly right. The screw speed would be quite a factor since under these conditions you would be adding various degrees of shear refining to the material as it enters the die.

A. Rudin: I wish I had said that.

C. Sadr: Is it generally true that the die swell for an incompatible system is higher than for a compatible one?

A. Rudin: I think that if you have an incompatible system, that is, if you have a polymer to which you add a small amount of another, incompatible one, you will reduce the melt elasticity, not increase it. So the extrudate swell should be lowered by incompatibility, not enhanced.

C. Sadr: Did you study the microstructure of the extrudates? Have you tried to add block polymers to the miscible systems?

A. Rudin: Block polymers have a big influence on the domain size of the dispersed phase and therefore have a bigger influence on the mechanical properties than on the chemical makeup of the blend. We did not study the microstructure of these blends.

Rheological and Mechanical Properties of Ternary Blends of Linear-Low-Density Polyethylene/Polypropylene/ Ethylene-propylene Block Polymers

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The effect of addition of an ethylene-propylene block polymer on rheological and mechanical properties of a linear-low-density polyethylene/polypropylene blend was examined. The samples were prepared by melt blending in a twin-screw extruder followed by injection molding. The single-, two- and three-component systems were treated the same way. The mechanical behavior of the blends was evaluated by means of tensile, and flexural, tests at 23 and -40°C . The capillary, elongational, and dynamic-flow measurements were performed at 190°C .

INTRODUCTION

The applicability of polymer blends is mostly limited by poor mechanical behavior resulting from incompatibility. A lack of adhesion at the interface is considered responsible for inferior performance. Despite these limitations, many of these blends have been prepared and used commercially. The possible solutions to the problem of incompatibility are: addition of a cosolvent or compatibilizer, mechanical compatibilization in a high shear blender, and orientation of the finished product by which the interphase boundary would be highly developed [1, 2].

Polyolefins are the principal commodity thermoplastics. Their blends have attracted much interest [3]. In particular, blends of polyethylene, PE, and polypropylene, PP, have been the subject of several investigations [3 to 6]. One reason for this is that these plastics constitute a significant percentage of plastics waste. Their recycling by blending is of substantial environmental and economic importance. In Canada, production capacity of linear-low-density polyethylene, LLDPE, will increase from 335 in 1983 to 1220 kt/yr by the end of 1986. Broadening the application of this resin is of significant national interest.

Blend properties often show complex behavior, depending on several factors. Admittedly, incompatibility causes a deterioration of properties due to the two-phase structure. However, the presence of the second phase might also bring about changes in the spherulite size, in total crystallinity, etc. These effects are not readily predictable.

In the first part of this study [7] the properties of binary LLDPE/PP blends were described. In this

second part we report on the effects of addition of a compatibilizer on the rheological and mechanical properties of these blends. It has been suggested that the use of a compatibilizer might be an answer to the disadvantages of a two-phase structure [8, 9]. The third component should promote adhesion at the interphases by creating intercrystalline links and tie molecules. It is generally believed that this can be best accomplished by addition of block polymers, whose parts are compatible with the different phases in the blend.

Experimental

Materials

The systems whose behavior will be reported here are based on gas-phase polymerized linear-low-density polyethylene, LLDPE, blended with PP with and without a block polymer of the type PE/PP/PE. The properties of the resins are listed in Table 1. Three different blends were prepared, all containing LLDPE and PP in a 1 to 1 ratio. In the basic blend of LLDPE/PP, BL, compatibilizers were not used. Blends BL-1 and BL-2 both contain 10 weight percent of the block polymer EP-1 and EP-2, respectively. To all samples 0.2 weight percent of antioxidants (a 1 to 1 blend of Irganox 1010 and 1024) was added. Blending was done in a Werner and Pfleiderer twin-screw extruder (Model ZSK-30) at 235°C . The resulting materials were granulated. The samples for tensile and flexural tests were injection molded in an Engel injection press (Model ES-170-50) using a single-gated mold, the injection following the sample axis. The sprues and runners were granulated and used in the rheological studies.

Table 1. Properties of the Resins.

Property	LLDPE	PP	EP-1	EP-2
Density (Kg.m ⁻³)	918	904	901	897
Melt index				
M.I. (g/10 min)	1.0	4.0	5.0	0.5
Molecular weights				
M_n ($\times 10^{-3}$)	97.5	250	—	—
M_w ($\times 10^{-3}$)	261	325	—	—
% Ethylene	—	—	11%	14%
Manufacturer	Union Carbide	Hercules	Hercules	Hercules

Rheological Testing

The Rheometrics Mechanical Spectrometer, RMS, Model 605, was used in dynamic and continuous shear modes at 190°C. The samples were premolded at 170°C into circular plates with diameters of 2.5 or 5 cm. For each sample, first the strain, γ , and the time, t , scans were done at two frequencies, $\omega = 1$ and 10 rad/s. In all cases the linear viscoelastic region was found. Next, the storage and loss moduli, G' and G'' , respectively, were determined within the frequency range of $\omega = 10^{-2}$ to 10^2 rad/s [10].

The elongational viscosity, η_e , was measured at 190°C in the Rheometrics Extensional Rheometer, RER. The instrument was used in constant stress, σ_{11} , and constant strain rate modes. The samples were transfer molded under vacuum, annealed, and then affixed with epoxy to the aluminum ties. For the tests, the samples were mounted in the instrument and immersed in a stationary silicone oil (Dow 200) at $T = 190.0 \pm 0.1^\circ\text{C}$ [11].

The high rate of shear, $\dot{\gamma}$, steady-state flow properties were measured in an Instron Capillary Rheometer (Model 3211), ICR, at 190°C. Two series of capillaries of different diameter were used in order to apply the three principal corrections: Rabinowitsch, Bagley, and Mooney [10, 12].

Mechanical Testing

The tensile (ASTM-D638) and flexural (ASTM-D790 method I) properties of all materials were measured at $T = 23$ and -40°C , using an Instron Universal Tensile Tester, Model 1125. Prior to testing, the injection-molded samples were conditioned at 23°C and 50 percent R.H. for at least 48 hours. The crosshead speed $V = 2.8$ mm/min was used for all except the tensile tests at 23°C, for which $V = 100$ mm/min was employed. The support span for flexural tests was 100 mm.

RESULTS

Melt Behaviour

Thermal stability

All samples were tested in RMS-time sweeps to judge the stability. As before [2], the derivative:

$$D = -10^3(\partial \ln G' / \partial t), \quad \omega = 10; \quad t \leq 60 \text{ min}; \quad (1)$$

was used for this purpose. The values of D are listed in Table 2. It can be seen that in the worst case (PP)

the sample was stable (decrease in G' of less than 2 percent) for 3 min while for the others it was stable for at least 30 min.

Strain sweep

Strain sweep within the range of $\gamma = 0$ to 40 percent, was done. At $\omega = 10$ rad/sec the most sensitive rheological parameter, G' , was found to be stable at $\gamma < 20$ percent. For this reason the dynamic tests were carried out at two strains: $\gamma = 10$ percent for $\omega = 10^{-1}$ to 10^2 and $\gamma = 20$ percent for 10^{-2} to 10^{-1} rad/sec.

ICR Flow

To start, the effect of die diameter should be examined. The results: η versus $\dot{\gamma}$, from two series of capillaries are shown in Fig. 1. The curves for BL-1 and BL-2 have been displaced by a factor of 5 and 10, respectively. In both cases, the points from different capillary diameters follow a single dependence.

There are three possible sources of variation of data computed from sets of capillaries of different diameter: slip on the wall, shear-induced crystallization, and shear modification of liquid structure. The superposition of data for BL-1 and BL-2 indicates absence of slip or shear modification of the blend morphology. For BL the data tend to separate

Table 2. The Properties of PE/PP Blends.

No.	Property	LLDPE	PP	BL	BL-1	BL-2
1	Composition	PE	PP	PE-50% PP-50%	BL-90% EP-1-10%	BL-90% EP-2-10%
2	D (min ⁻¹)	0.4	6.54	0.53	0.32	0.80
3	θ	0.078	0.111	0.151	0.139	0.162
4	R ($\omega = i = 10^{-1}$)	1.268	1.184	1.249	1.329	1.389
5	M_w/M_n	0.8	4.5	2.4	2.7	2.6
6	$\eta_0 \times 10^{-3}$ (Pa.s)	2.0	7.2	4.8	5.2	6.3
7	$\eta_{sc} \times 10^{-3}$ (Pa.s)	10.2	8.8	12	14.6	17.0
8	$\eta_w/3000$ (Pa.s)	13.0	8.1	14.2	15.6	16.7

Notes: (a) 0.2 percent of a mixture of Irganox 1010 and 1024 was added in all cases; (b) calculated using dependencies proposed by Zeichner and Patel [12]; (c) from Cole-Cole plot.

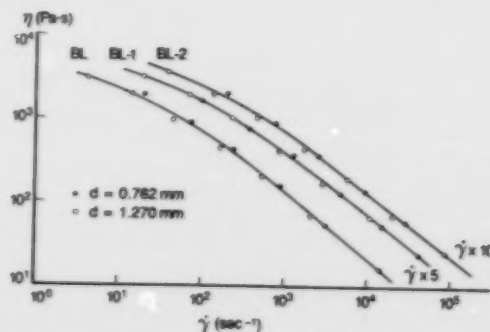


Fig. 1. Shear viscosity versus shear rate for BL, BL-1, and BL-2 at 190°C. Data for BL-1 and BL-2 have been displaced on the x-axis by a factor of 5 and 10 respectively.

as the shear rate decreases. One cannot invoke wall slip as responsible for this segregation; usually this effect increases with $\dot{\gamma}$. The remaining source of variation, the shear modification of blend morphology, seems to be the only possible explanation left. Looking at the dependence one notices that viscosities from the smaller capillary diameter are higher indicating a higher degree of dispersion obtained at this higher convergence ratio. One may infer that BL is not as thermodynamically stable a blend as BL-1 and BL-2.

Another useful method for analyzing the capillary flow [10] is to plot the Bagley correction, P_e , as a function of the shear stress, σ_{12} , (viz. Fig. 2). Again BL-1 and BL-2 data give well-defined single dependencies. However, similar to that in Fig. 1, the data for BL at low values of σ_{12} fall on two dependencies, confirming the suspected morphological source of deviation.

Dynamic flow

The data, taken as previously described, are presented in Figs. 3 to 7. Both the complex η^* , and dynamic η' , viscosities are presented. For LLDPE

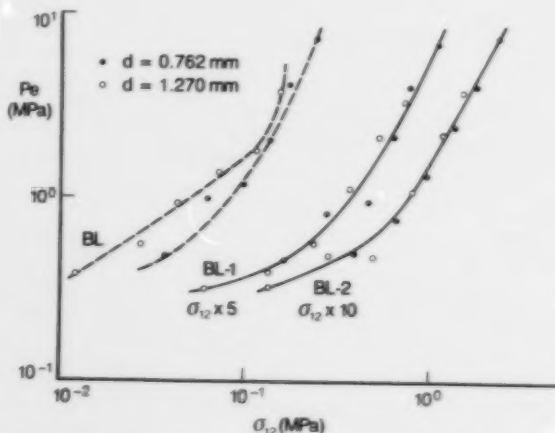


Fig. 2. Bagley pressure correction term, P_e , versus shear stress, σ_{12} , for BL, BL-1, and BL-2. Data for BL-1 and BL-2 have been displaced on the x-axis by a factor of 5 and 10 respectively.

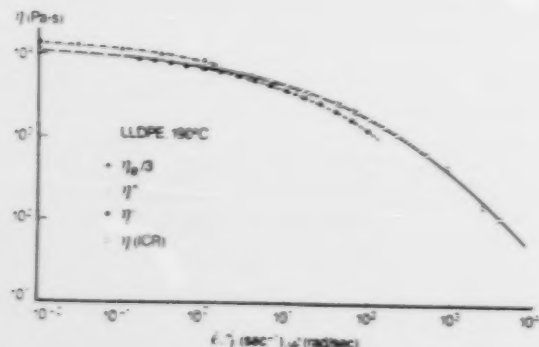


Fig. 3. Elongational, η_e , complex, η^* , dynamic, η' , and shear, η , viscosities versus strain rate, $\dot{\epsilon}$, frequency, ω , or shear rate, $\dot{\gamma}$, for LLDPE at 190°C.

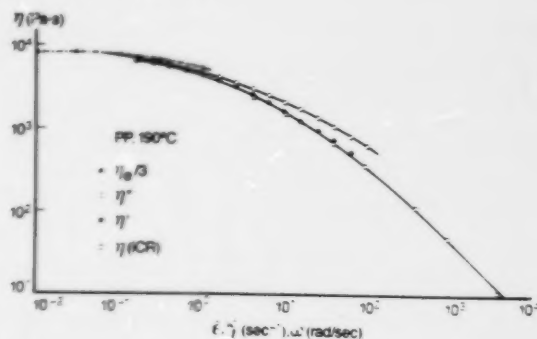


Fig. 4. Elongational, η_e , complex, η^* , dynamic, η' , and shear, η , viscosities versus strain rate, $\dot{\epsilon}$, frequency, ω , or shear rate, $\dot{\gamma}$, for PP at 190°C.

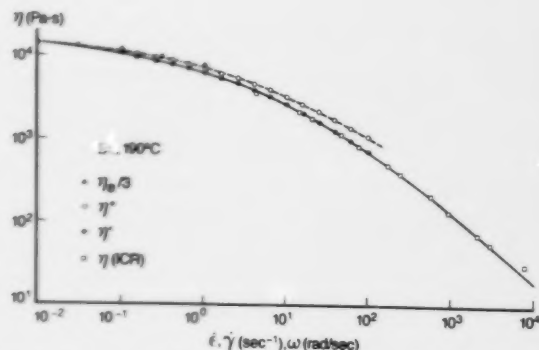


Fig. 5. Elongational, η_e , complex, η^* , dynamic, η' , and shear, η , viscosities versus strain rate, $\dot{\epsilon}$, frequency, ω , or shear rate, $\dot{\gamma}$, for BL at 190°C.

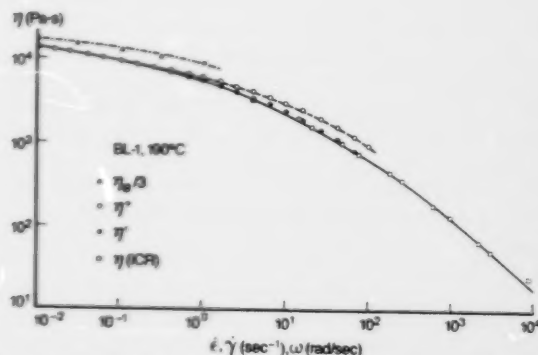


Fig. 6. Elongational, η_e , complex, η^* , dynamic, η' , and shear, η , viscosities versus strain rate, $\dot{\epsilon}$, frequency, ω , or shear rate, $\dot{\gamma}$, for BL-1 at 190°C.

(Fig. 3) at the higher range of rates of deformation, $\omega = \dot{\gamma}$, the $\eta(\text{ICR}) = \eta'$, whereas at lower range $\eta(\text{ICR}) = \eta^*$. This behavior was reported before [10]. For PP (Fig. 4) the capillary data (corrected for shear crystallization) fall on the η' versus ω curve in the full range of overlapping rates of deformation. The blends BL, BL-1, and BL-2 indicate a behaviour similar to PP (Figs. 5 to 7): in all cases the capillary data coincide with the η' versus ω dependence. Note that the shear crystallization was not observed for blends and the capillary data were

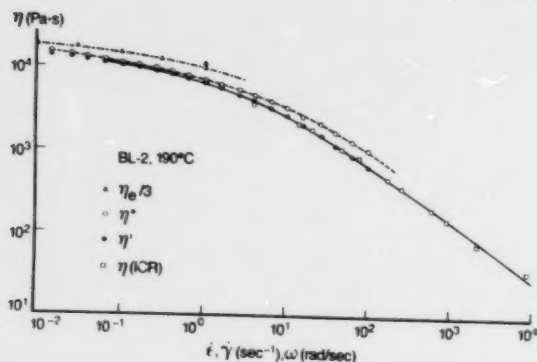


Fig. 7. Elongational, η_e , complex, η^* , dynamic, η' , and shear, η'' , viscosities versus strain rate, $\dot{\epsilon}$, frequency, ω , or shear rate, $\dot{\gamma}$, for BL-2 at 190°C.

corrected only by Bagley and Rabinowitsch procedures.

The storage modulus, G' versus ω , for all five samples is presented in Fig. 8. The highest G' at low ω is obtained for BL-2, and at high ω for LLDPE.

Elongational flow

The stress growth function η_e^+ versus time, t (sec), for the five samples is shown in Fig. 9. In all cases the dependence is similar, with a low slope:

$$\theta = \partial \ln \eta_e^+ / \partial \ln t, \quad t = 1 - 100s, \quad (2)$$

and with no sign of stress hardening. During these tests it was observed that deformation of LLDPE and PP was uniform throughout the elongation at all $\dot{\epsilon}$. The low viscosity PP at low values of $\dot{\epsilon} < 0.1 s^{-1}$ generated such a low force that the tests were discontinued at a relatively low value of the Hencky strain $\epsilon = 1$ to 2. At higher rates of deformation the equipment limited stretch-ratio ($\epsilon = 3.1$) was obtained (for all resins) without a break. Deformation of the blends BL, BL-1, or BL-2 was not always uniform.

It has been observed [11] that the slope θ can be used as a measure of sample polydispersity. The average values of θ within the time range 1 to 100 sec are listed in Table 2. Judging by the larger values of θ for the blends (than those for the neat resins) one has to postulate at least a partial compatibility.

In Fig. 9 the stress-growth functions, measured at $\dot{\gamma} = 10^{-2} (s^{-1})$ at 190°C in a cone-and-plate geometry (5-cm diameter) are also shown. An excellent correlation between the two sets of data from RER and RMS is observed. The maximum plateau value of η^+ at each $\dot{\epsilon}$ can be taken as the equilibrium elongational viscosity, η_e . These values are plotted in Figs. 3 to 7 as $\eta_e/3$ vs. $\dot{\epsilon}$. The Trouton ratio can be defined as:

$$R = \eta_e/3\eta = \eta_e/3\eta' = \eta_e/3\eta^*; \quad \omega = \dot{\gamma} = \dot{\epsilon} \quad (3)$$

The values of R at the rate of deformation $\omega = \dot{\epsilon} = 0.1$ are listed in Table 2. Judging by their magnitude, the closest to the Newtonian plateau is PP and the furthest BL-2. This is another indication of an effective broadening of the apparent polydispersity of the samples.

Mechanical Properties

Tensile Testing

From the engineering stress-strain curves (Fig. 10), Young's modulus, E , was calculated as the tangent to the initial straight-line portion of the curve. The maximum values of the elongation and stress, ϵ_{max} and σ_{max} , respectively, were computed

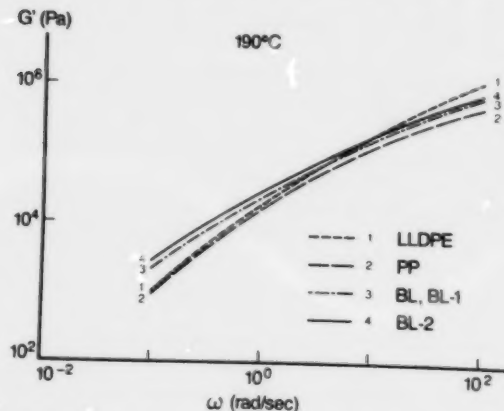


Fig. 8. Storage modulus, G' , versus frequency, ω , for LLDPE, PP, BL, BL-1 and BL-2.

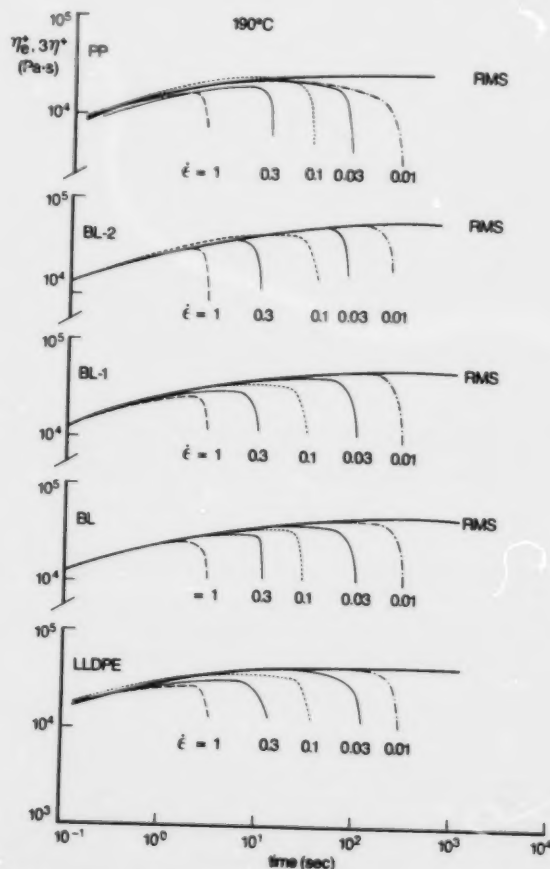


Fig. 9. Comparison of shear, $3\eta'$, and elongational, η_e^+ , time-dependent viscosities for PP, BL-2, BL-1, BL, and LLDPE at 190°C.

as well. The results are presented in Table 3 and Figs. 11 and 12, as functions of the composition. In the graphs, the solid lines are drawn to represent the data of one and two component systems without the compatibilizer. The broken lines illustrate the simple additivity rule.

It can be seen (Fig. 11) that at 23°C, E for the blends is significantly higher (by 27 to 41 percent) than the additivity rule would predict. At -40°C, i.e. above the glass transition temperature, T_g , of LLDPE, but below T_g of PP, the results for BL follow the additivity rule, while those for BL-1 and BL-2 show a positive deviation. It is clear that addition of EP improves the performance at ambient as well as at low temperature.

In Fig. 12 the maximum stress computed as:

$$\sigma_{\max} = F_{\max}/A_0 \quad (4)$$

(where $F_{\max}$ is the maximum recorded force and A_0 is the initial cross-sectional area of the specimen) is presented. Again, an improvement of properties upon addition of either EP-1 or EP-2 is noted.

The numerical values of E , $\sigma_{\max}$, and the Hencky strain at break, $\epsilon_{\max}$, are listed in Table 3. At 23°C the only break observed was for PP; the remaining samples did not break up to the experimentally accessible limit $\epsilon = 1.34$. At -40°C this limit was lowered to $\epsilon = 0.53$; in this case only LLDPE did not break. It is evident that addition of the compatibilizer improves the modulus and maximum strength at the cost of a decrease in the maximum strain. In relation to BL the $\epsilon_{\max}$ of BL-1 and BL-2 decreased respectively by 29 and 33 percent.

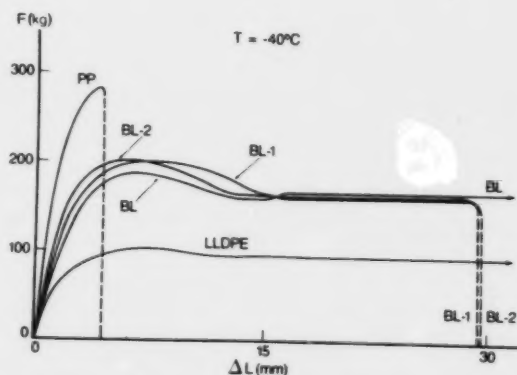


Fig. 10. Stress-strain curve from tensile testing for PP, BL-1, BL-2, BL, and LLDPE at -40°C.

Flexural Testing

The bending modulus, E_b , and the maximum fiber stress, S , were calculated as specified in ASTM-D790. These values are presented in Fig. 13 and Table 3. A small improvement in E_b was obtained for the compatibilized blends. However, the effect of EP-1 and EP-2 is negligible as far as S is concerned.

DISCUSSION

As reported in Table 2 the degradation rates for all but PP samples are relatively low, resulting in 1 to 2 percent reduction of G' during 30 min of testing. In the case of PP the reported 20 percent reduction during the same period of time is significant; it could be halved by changing the test environment from air to nitrogen, but not eliminated. For this reason the data for PP were determined from scans done in two directions. The stabilizing effect of LLDPE on PP is worth noting.

In the capillary flow of PP the effect of shear crystallization was observed and corrected using the Mooney method. In the presence of LLDPE the data followed a single η versus $\dot{\gamma}$ curve, independent of the capillary diameter. These curves are reproduced in Fig. 14. It is interesting to note that in spite of almost a decade of difference in the viscosities of neat polymers, there is no evidence of shear de-mixing in any of the three blends. In fact, within the full range of $\dot{\gamma}$ their flow curves are the same within the range of experimental error.

As observed in ICR data, the dynamic flow indicate a similar behavior for all three blends. In Fig. 8 G' for BL and BL-1 follow the same curve, while for BL-2 it is higher by only about 15 percent. At low ω the storage moduli for the two neat polymers are nearly identical, while those for the blends are about 3-fold higher and similar to each other. The higher G' values of BL-2 may indicate a better dispersion or an influence of higher G' of the block polymer EP-2.

It has been reported [13, 14] that in PP the crossover point $G_c = G' = G''$ at $\omega = \omega_c$ is a measure of the molecular weight, M_w , and the molecular weight distribution, M_w/M_n . This observation was confirmed in our laboratory for neat polypropylene and polyethylene resins [10, 15]. In Fig. 15 the values G_c versus ω_c are plotted for the five examined samples. Assuming that the relations given by the authors [13] for PP can provide a measure of

Table 3. Mechanical Properties of Materials.

Type of Tests	Property	T (°C)	LLDPE	PP	BL	BL-1	BL-2
Tensile	E (GPa)	23	0.241	1.25	0.947	1.05	1.03
		-40	1.38	3.16	2.26	2.55	2.60
	$\sigma_{\max}$ (MPa)	23	9.88	34.5	20.7	21.4	21.4
		-40	24.1	68.8	46.3	49.6	49.8
	$\epsilon_{\max}$	23	>1.34	0.871	>1.34	>1.34	>1.34
		-40	>0.50	0.05	0.33	0.25	0.24
Flexural	E_b (GPa)	23	0.245	1.24	0.545	0.590	0.582
		-40	1.21	3.31	2.16	2.23	2.22
	S (MPa)	23	8.22	38.3	17.5	17.5	17.5
		-40	34.6	107	68.2	68.9	67.0

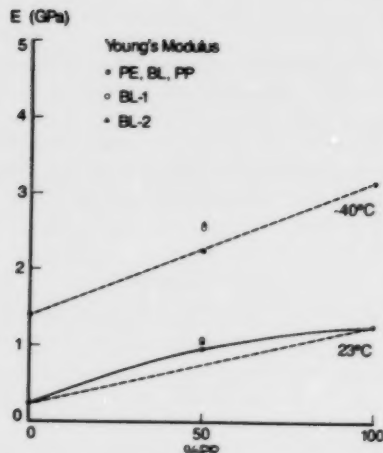


Fig. 11. Young's modulus, E , versus composition at 23°C and -40°C.

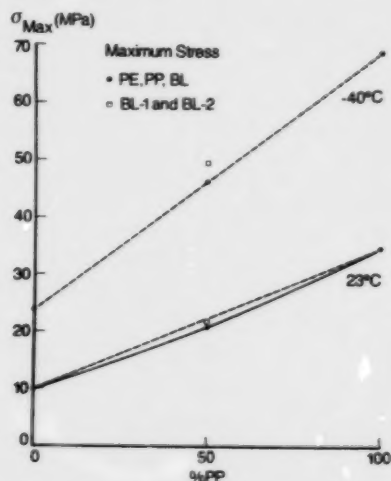


Fig. 12. Maximum stress, σ_{max} , versus composition at 23°C and -40°C.

changes in effective $\overline{M}_w/\overline{M}_n$ and η_0 , the values quoted in Table 2 were calculated. It is interesting to see that G_c and ω_c for the blends are dominated by PP—the lower viscosity component. The values of $\overline{M}_w/\overline{M}_n$ are not in agreement with the information provided by the slope θ ; whereas the stress growth indicates increased polydispersity on blending, $\overline{M}_w/\overline{M}_n$ do not seem to be valid for blends.

In Fig. 16 the Cole-Cole plot of η'' versus η' for the blends is presented. Since the curves up to the maximum value of η'' are semicircular, one can use them to determine the zero shear viscosity $\eta_{oc} = \eta'(\eta'' = 0)$. These values are also given in Table 2. Comparing η_{oc} and $\eta_0/3$ with η_0 calculated from G_c and ω_c , one can see that while the value for PP is relatively close, those for the other samples are significantly different; i.e. the Zeichner and Patel method should not be used for the blends.

In conclusion, the melt rheology indicates a partial compatibility of the LLDPE/PP blends, with or without the block polymer. The ICR results for BL at low $\dot{\gamma}$, the nonuniformity of deformation in RER

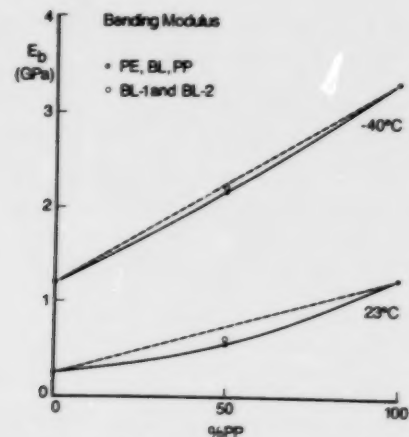


Fig. 13. Bending modulus, E_b , versus composition at 23°C and -40°C.

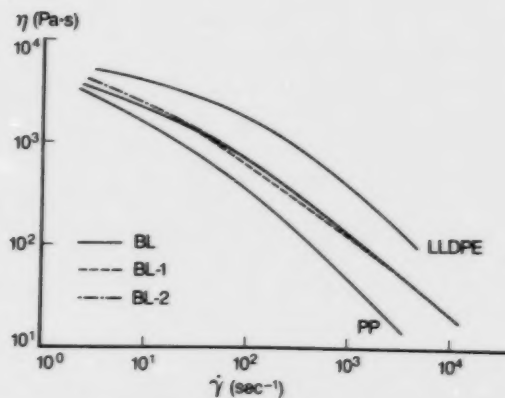


Fig. 14. Comparison of shear viscosity, η , versus shear rate, $\dot{\gamma}$, for LLDPE, BL, BL-1, BL-2, and PP at 190°C.

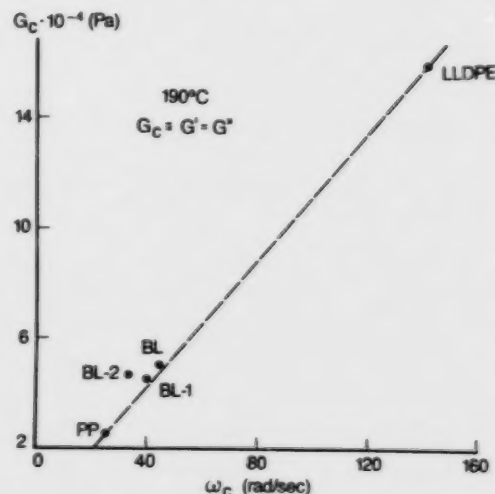


Fig. 15. Coordinates of $G' = G''$ cross-over point: G_c , versus ω_c , for LLDPE, BL, BL-1, BL-2, and PP at 190°C.

and the nonadditivity of θ , R , and η_0 (see Table 2) all indicate that these blends belong to the PDB family [2].

The mechanical properties of polyolefin blends: LDPE/HDPE, LDPE/PP, HDPE/PP as functions of composition and molecular weight, MW, were recently reported [16, 17]. The results indicate a phase separation in all but the blends of low MW HDPE/PP. The authors reported that the highest enhancement of properties (synergism) was obtained for HDPE/PP, with PP of high MW (melt index = 0.4 g/10 min).

The blends evaluated in this paper can be compared with the high MW HDPE/low MW PP investigated earlier [17]. The enhancement of properties seen in Figs. 11 and 12 is in agreement with the previous results. However, the maximum enhancement of properties should be expected not at weight ratio PE to PP equal 1 to 1 but rather 4 to 1. In other words, for practical use the improvements of LLDPE properties are expected to be larger at the higher LLDPE content than those reported here.

Figs. 11 to 13 illustrate that the properties of BL are averages of those of the neat resins. Addition of block polymers improves the moduli, and maximum stress at break, in particular at -40°C . It should be stressed that the improvement of the low temperature performance is the key to a practical application of the blends. In Figs. 10 and 17 the copies of tensile and flexural test traces at -40°C are reported. The improvement of performance is clearly indicated. While PP shows a brittle fracture and LLDPE a very low maximum stress, the blends demonstrate a ductile behaviour with a significant improvement of the maximum strength at break.

The main difference between the two block polymers is the molecular weight. Since values of the melt index for PP and EP-1 are similar (viz Table I), their MW is expected to be of the same order of magnitude. The second block polymer, EP-2, shows a lower value of melt index and, therefore, this MW is higher. Nevertheless the behaviour of BL-1 and BL-2 is similar. In most cases the discrepancies between these two materials are of the order of the

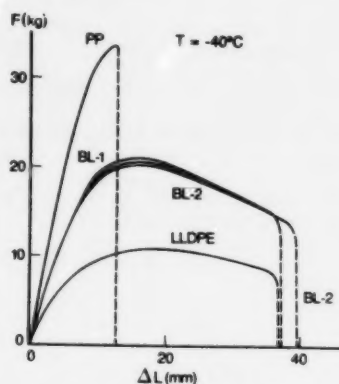


Fig. 17. Stress-strain curve from flexural testing for PP, BL-1, BL-2, and LLDPE at -40°C .

experimental error. Judging by the performance during mechanical testing, we cannot see any effect of the MW on the compatibilizing ability of the block polymer. However, the presence of the longer chains of EP-2 affects the melt flow, e.g. BL-2 tend to give higher viscosity than BL-1 at low rates of deformation (viz Fig. 14 and values of η_0 in Table 2). Higher degree of entanglement in BL-2 is expected and may explain the larger values of G' observed for low ω in Fig. 8.

CONCLUSIONS

The addition of block polymer increases rigidity, strength, and brittleness. The MW of the block polymer does not play a significant role in the mechanical performance.

Melt rheology indicates: a partial compatibility of LLDPE/PP blends with or without block polymer; and a stabilizing effect of the block polymer on two-phase structure.

ACKNOWLEDGMENT

The authors would like to thank Mr. P. Sammut for his careful work collecting the rheological data.

REFERENCES

1. NRCC-IMRI mini-symposia "Polymer Blends-'81", *Polym. Eng. Sci.*, **22**(2) (1982); "Polymer Blends-'82", *ibid.*, **22**(17) (1982); "Polymer Blends-'83", *ibid.*, **24**(2) (1984).
2. L. A. Utracki and M. R. Kamal, *Polym. Eng. Sci.*, **22**, 96 (1982); L. A. Utracki and G. L. Bata, *Matériaux Tech. (Paris)*, **70**, 223, 282 (1983); L. A. Utracki, *Polym. Eng. Sci.*, **22**, 116 (1982); *ibid.* **23**, 602 (1983); L. A. Utracki, *Polym. Plast. Technol. Eng.*, **22**, 27 (1984).
3. A. P. Plochocki, Ch. 21 in "Polymer Blends", D. R. Paul and S. Newman (Eds.), Academic Press, New York (1975).
4. A. J. Lovinger and M. L. Williams, *J. Appl. Polym. Sci.*, **25**, 1703 (1980).
5. R. E. Robertson and D. R. Paul, *J. Appl. Polym. Sci.*, **17**, 2579 (1973).
6. R. D. Deanin and G. E. D'Isodoro, *Am. Chem. Soc., Org. Coat. Plastics Chem. Prepr.*, **43**, 19 (1980).
7. M. M. Dumoulin, L. A. Utracki, and C. Farha, *SPE ANTEC Tech. Papers*, **30**, 443 (1984).
8. E. Nolley, J. W. Barlow, and D. R. Paul, *Polym. Eng. Sci.*, **20**, 364 (1980).
9. T. D. Traugott, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **28**, 2947 (1983).
10. L. A. Utracki and R. Gendron, *J. Rheology*, **28**, 601 (1984).

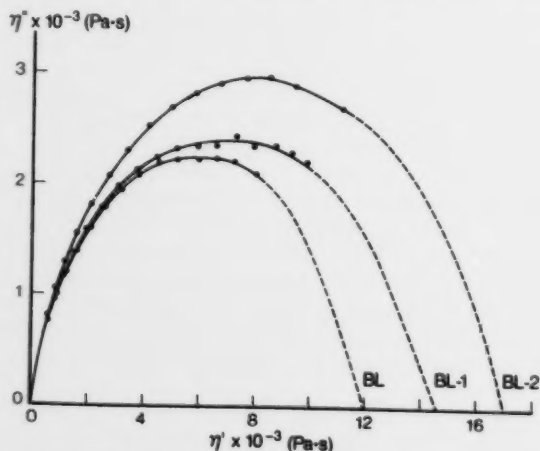


Fig. 16. Imaginary part, η'' , versus real part, η' , of the complex viscosity for BL, BL-1, and BL-2.

11. L. A. Utracki, Paper presented at the Int. Congress on Rheology, Acapulco, Mexico, Oct. 8 to 13, 1984. *Proceedings*, Vol. 3, p. 567.
12. R. Darby, "Viscoelastic Fluids," Ch. 5, Marcel Dekker, Inc., New York, N.Y. (1976).
13. G. R. Zeichner and P. D. Patel, Paper presented at 2nd World Congress of Chemical Engineering, Montreal, Canada, Oct. 1981.
14. G. R. Zeichner and C. W. Macosko, *Proceed. IUPAC 28th Macromolecular Symposium*, Oxford, U. K., 1982, p. 861; *SPE ANTEC Tech. Papers*, 28, 79 (1982).
15. M. M. Dumoulin, L. A. Utracki, and J. Lara, *Polym. Eng. Sci.*, 24, 117 (1984).
16. M. F. Sansone, M.Sc. Thesis, University of Lowell, 1977.
17. G. E. D'Isidoro, M.Sc. Thesis, University of Lowell, 1979.

DISCUSSION

G. Vexler: I understand that it would be difficult but you should try to identify the morphology of your samples. It will be interesting to see to what extent PP is miscible with LLDPE and what is the effect of the block polymer addition.

M. M. Dumoulin: I agree with you that we need more information on the morphology. This part of the study is already started but is far from completion. We definitely plan to work in this direction in the near future.

C. Sard: We observed that the mechanical properties of blends not stabilized by block polymers are very poor. To get any use of the blend we have to add 10 to 15 percent of copolymer. I am surprised to see how small is the effect of the block polymer on the mechanical performance of your blend.

M. M. Dumoulin: The reason why the effect of the block polymer is not very important might be that the two polymers were selected on the basis of similarity of their melt index. On the other hand the fact that molecular weight of EP does not play any apparent role may indicate that it was not properly dispersed.

P. Carreau: You showed a very rapid drop of the stress-growth function; in your slide the function reached a plateau defining the elongational viscosity and then dropped very rapidly. How do you explain this?

M. M. Dumoulin: The graph which you are referring to shows $\log \eta_e^+$ variation with $\log t$. At constant strain rates the stress-growth function for all five samples increased up to a plateau level, held at this value for a time, and then the sample started to break. The rapid decrease which you are referring to is the trace of stress during breaking. Physically, during this time, the sample starts to deform non-uniformly, necking down to nothing on a relatively small sample length during the period of time indicated on the figure.

L. A. Utracki: I would like to add a comment to this response. During the last two weeks, Pierre Sammut repeated the extensional viscosity measurements this time using the constant-stress mode. This is a very useful method of determination of the

equilibrium extensional viscosity. Usually the strain increases linearly with time allowing quite precise calculation of the strain rate. Since σ_{11} is constant, the η_e can be easily determined. These values of η_e agreed very well with those determined from the plateau levels of the stress growth functions shown by Michel Dumoulin. In other words, the plateaus obtained during the steady rate of straining experiments reflect the equilibrium conditions, prior to breakage. On another subject, I hope that you realize that we have here a report on a new, previously unpublished system: polypropylene blended with linear-low-density polyethylene, which in fact is a copolymer of ethylene with higher (most likely 1-butene) olefin(s). Our results show that this system behaves differently than those previously reported: LDPE/PP or HDPE/PP. Even prior to addition of EP the blend, BL, in the molten and solid states showed an average performance which could be calculated from properties of the pure resins. Since the performance was already relatively good, the addition of EP did not affect it greatly. This may be an indication of at least a partial compatibility of PP and LLDPE, deduced from the rheological measurements but so far unconfirmed by direct morphological study.

M. R. Kamal: Could you tell us how the samples for mechanical testing were prepared.

M. M. Dumoulin: All the materials were blended in a twin screw extruder (Werner-Pfleiderer ZSK-30), granulated, and injection molded. We used a single-gated mold. The gating being at one end of the sample, the injection followed the axis of the test bar.

M. R. Kamal: Depending on the viscosity of your two resins you may get a shape effect in the sample. In some cases a fibrillar structure may develop in which the fibers play a reinforcement role, as in fiber reinforced polymer composites. You are trying to interpret all your results from the point of view of compatibility, whereas I wonder if enough attention was given to the other effects, namely the morphology of the prepared samples and the geometrical factors of the two resin domains.

M. M. Dumoulin: We did see some fibrillation in the samples broken during tensile and flexural tests. However, I do not think that here the domain geometry plays an important role. We have done some temperature cycling on selected blend samples, raising their temperature to 100°C and then letting them slowly cool over a period of three to four hours. After such cycles the samples showed slightly increased moduli and maximum strength and a corresponding decrease of the maximum strain at break. These data can be taken as evidence, on one hand, of an enhanced degree of crystallinity due to cycling and, on the other, of an insignificant effect of the original blend structure generated during the injection molding.

Development of Phase Morphology in Incompatible Polymer Blends during Mixing and its Variation in Extrusion*

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An experimental study of the development of phase morphology in incompatible polymer melt blends of polyethylene/polyethylene (PE/PS), polyethylene/polycarbonate (PE/PC), and polyethylene/nylon-6 (PE/N6) is presented. Different temperatures (180°C, 240°C) of mixing and polyethylene molecular-weight levels were used in the PE/PS studies. Little variation in the cross-sectional phase morphology of the PE/PS extrudates was observed with these variables, though the morphology became finer with increased shear rate/stress in capillary die flow. Variations in the longitudinal morphology are observed with continuous filaments of dispersed phase only arising when the dispersed phase has an equal or lower viscosity than the continuous phase. The PE/N6 and PE/PC, especially the former, give coarser morphologies when the N6 and PC are the continuous phases. This was attributed to larger interfacial tensions. The effect of viscoelasticity was also discussed.

INTRODUCTION

Polymer blends play an important role in commerce. The study of their formation and characteristics is of increasing importance and interest. There have been several studies in which the phase morphology of individual blend systems has been investigated as a function of flow or process conditions (1 to 11). There have, however, not been basic comparative studies of the influence of blending and process conditions with different pairs of polymer components except to look at the influence of molecular weight/viscosity (7, 8).

Most investigations generally discuss phase morphology variations in terms of shear stresses, disrupting domains, and forming fibrils. There has been some discussion of the influence of viscosity ratio on fibril stability. Most studies are limited to blends of a single polymer pair and do not contrast materials of varying composition and properties. In the present paper three systems, high-density polyethylene (PE)/polystyrene (PS), high-density polyethylene (PE)/polycarbonate (PC), and high-den-

sity polyethylene/nylon 6 (N6) were investigated. In the case of the PE/PS system, we consider three different polyethylenes of varying molecular weight and distribution. For the PE/PS system, studies were also carried out at two different temperature levels of mixing, 180°C and 240°C. These latter experiments were carried out because the change in temperature causes major variations in rheological properties of the polystyrene, notably viscosity decreases, but not the polyethylene.

EXPERIMENTAL

Materials

The polymers included in this study were three polyethylenes of varying molecular weight (PE-1, PE-2, PE-3), polystyrene (PS), nylon-6 (N6), and polycarbonate (PC). The characteristics of these polymers are summarized in *Table 1*. Shear viscosity—shear rate data are summarized in *Figs. 1a and b* at 180°C and 240°C. Principal normal stress difference—shear stress data are contained in *Figs. 2a and b*. Plots of this type are independent of temperature (12), but depend upon polymer structure (13).

* The experimental studies described were carried out at the University of Tennessee as part of the Ph.D. Dissertation of K. Min.

Table 1. Characteristics of Polymers Studied.

Material	Supplier	MI	η_0 (240°C) (poise)	η_0 (180°C) (poise)
			$\times 10^6$	$\times 10^6$
Polyethylene-1	Chemplex 6003	0.3	—	10.0
Polyethylene-2	Chemplex 6109	0.9	3.8	5.0
Polyethylene-3	Chemplex 6060	6.0	—	0.4
Polystyrene	Dow Styron 678U	12.0	0.1	3.2
Nylon-6	American Enka	—	0.057	—
Polycarbonate	General Electric	—	0.6	—

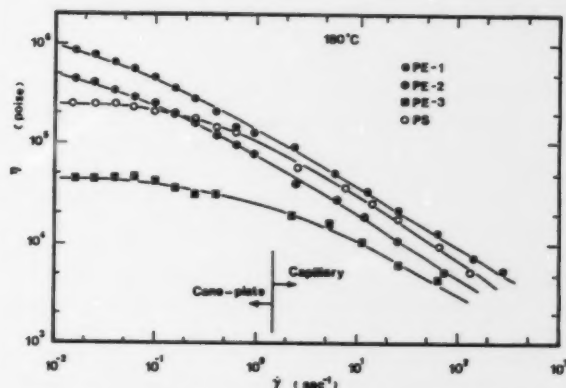


Fig. 1a. Shear viscosity-shear rate data for PE-1, PE-2, and PE-3 high-density polyethylene and polystyrene at 180°C.

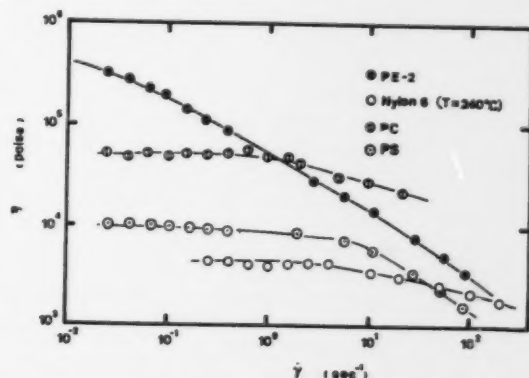


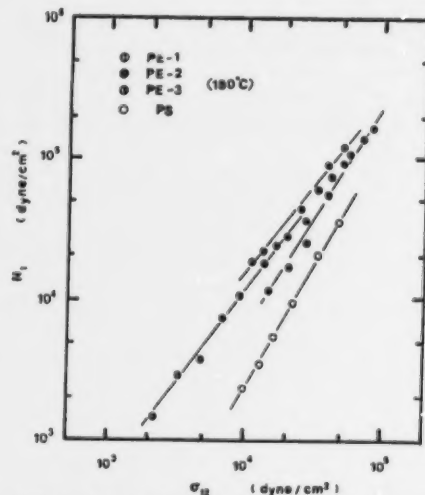
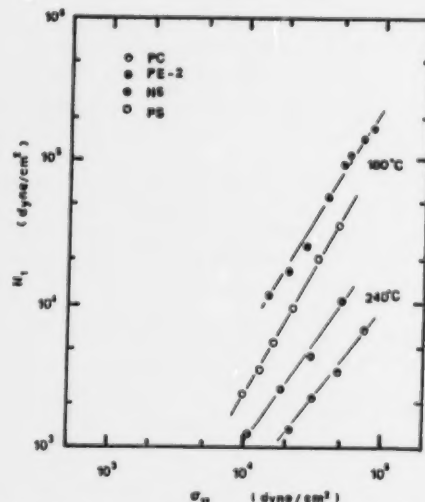
Fig. 1b. Shear viscosity-shear rate data for PE-2, nylon 6, polycarbonate, and polystyrene at 240°C.

Blending

The polymers in this study were blended together using a 3/4-inch Brabender screw extruder with a Koch static mixer. These were done in composition ranges defined in Table 2. The PE-1/PS, PE-2/PS, and PE-3/PS were blended at 180°C. The PE-2/PS was blended at 240°C. PE-2/PC and PE-2/N6 were blended at 240°C.

Phase Morphologies

The phase morphologies were determined using an AMR high-resolution scanning-electron microscope. Fracture surfaces were prepared in liquid nitrogen. In many cases the blend samples were extracted by using toluene.

Fig. 2a. Principal normal-stress difference, N_1 -shear stress σ_{12} plots for PE-1, PE-2, and PE-3 with PS.Fig. 2b. Principal normal-stress difference, N_1 -shear stress σ_{12} plots for PE-2, PS, N6, and PC.

Capillary Extrusion

The blend samples were extruded through capillary dies mounted in a Merz-Colwell Instron capillary rheometer. Dies with diameter of 1 mm (0.058 inch) and length/diameter ratios (L/D) of 10, 20, 30, and 40 were used in this study. This is the same apparatus as was used in our earlier investigations (10, 11).

RESULTS

Static Mixer

SEM photomicrographs of fracture surfaces of polyethylene/polystyrene extrudates produced by the static mixer are shown in Figs. 3 and 4. Figure 3 compares PE-1/PS, PE-2/PS, and PE-3/PS at 180°C. Figure 4 contains the phase morphologies of the PE-2/PS blends at 240°C. It may be seen that at high polyethylene levels the polystyrene is dispersed in a polyethylene matrix, and at high

Table 2. Blend Systems Investigated.

System	Compositions	Temperature of Investigation
Polyethylene-1/Polystyrene (PE-1/PS)	90/10, 70/30, 50/50, 30/70, 10/90	180°C
Polyethylene-2/Polystyrene (PE-2/PS)	90/10, 70/30, 50/50, 30/70, 10/90	180°C, 240°C
Polyethylene-3/Polystyrene (PE-3/PS)	90/10, 70/30, 50/50, 30/70, 10/90	180°C
Polyethylene-2/Nylon-6 (PE-2/N6)	90/10, 70/30, 50/50, 30/70, 10/90	240°C
Polyethylene-2/Polycarbonate (PE-2/PC)	90/10, 70/30, 50/50, 30/70	240°C

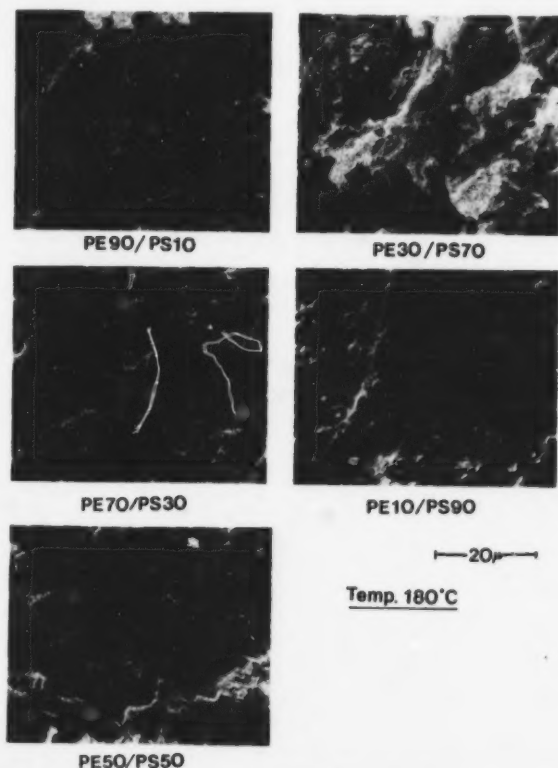


Fig. 3a. SEM photomicrographs of PE-2/PS blends from the static mixer at 180°C at various compositions: PE-1/PS, 90/10, 70/30, 50/50, 30/70, and 10/90;

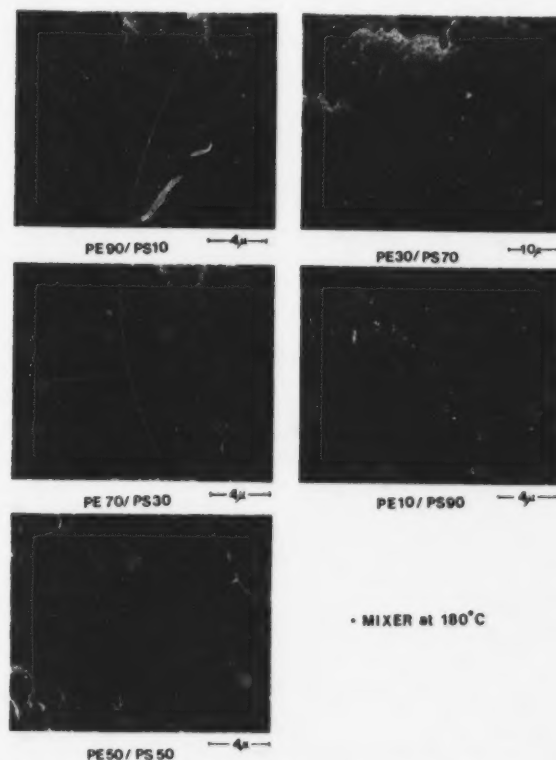


Fig. 3b. PE-1/PS, 90/10, 70/30, 50/50, 30/70, and 10/90;

polystyrene content the polyethylene is the dispersed phase. At intermediate compositions, co-continuous phases are obtained. Generally the phase dimensions are in the range of 1 to 10 μm . We have sought to quantify these results through the definition of number and weight-average disperse-phase dimensions:

$$d_n = \frac{\sum N_i d_i}{\sum N_i} \quad (1a)$$

$$d_w = \frac{\sum N_i d_i^2}{\sum N_i d_i} \quad (1b)$$

The values of d_n and d_w have been determined using 100 dispersed globules for each system. The values determined are summarized in Tables 3 and 4.

These results are plotted as a function of polyethylene content in Fig. 5.

SEM photomicrographs of polyethylene (PE-2)/nylon-6 (N6) and polyethylene (PE-2)/polycarbonates (PC) extrudates formed from the static mixer are shown in Fig. 6. At high PE-2 levels, the N6 is dispersed, while at high N6 levels the PE-2 is the dispersed phase. The PE-2 globules dispersed in the N6 are much coarser, i.e. they have larger dimensions than the N6 dispersed in the PE-2. The PE-2 dispersion in the N6 is coarser than the PE/PS blends described in the above paragraph.

SEM photomicrographs of polyethylene (PE-2)/polycarbonate (PC) extrudates from the static mixer show the same tendency as in polyethylene (PE-2)/nylon-6 (N6). The PE-2 globules dispersed in the PC are coarser than the PC globules dispersed in the PE-2. The PE-2/PC, PE-2/N6, and PE-2/PS globule size is plotted as a function of composition

in Fig. 7. The ordering of coarseness of PE-2 in co-continuous and dispersed matrices is clearly nylon-6 > polycarbonate > polystyrene.

Capillary Die

The polymer blends described in the previous section have been extruded through a capillary die at various extrusion rates and die-wall shear stresses which are corrected for entrance pressure losses.

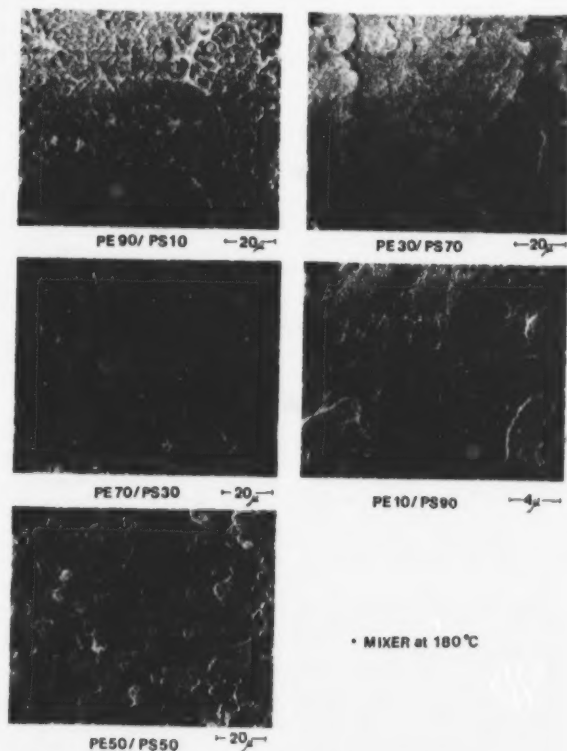


Fig. 3c. PE-3/PS, 90/10, 70/30, 50/50, 30/70, and 10/90.

Typical SEM photomicrographs of the extrudate cross sections are shown in Fig. 8 and the dispersed-phase dimensions are plotted as a function of die-wall shear stress in Fig. 9. Generally the morphology becomes increasingly fine grained as the die-wall shear stress increases. The effects are the greatest

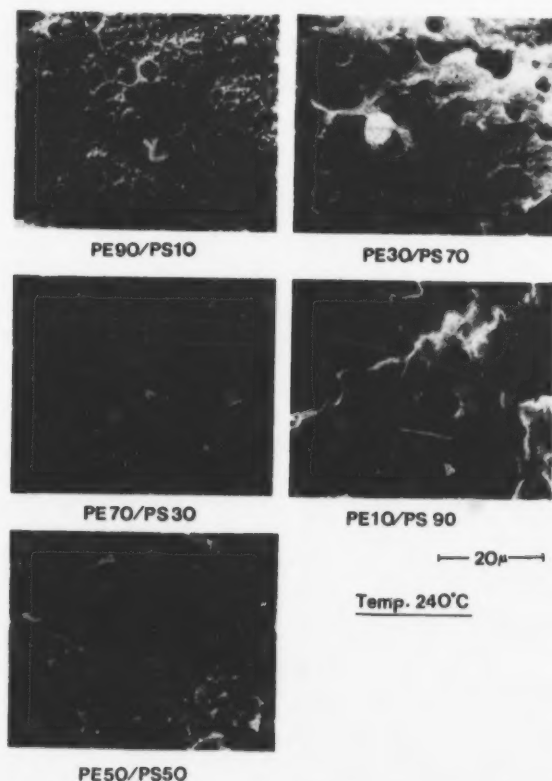


Fig. 4. SEM photomicrographs of phase morphology of PE-2/PS blends from static mixer at 240°C at various compositions: 90/10, 70/30, 50/50, 30/70, and 10/90.

Table 3. Dimensions of Discrete Phase of PE/PS Blends Prepared by Screw Extruder and Koch Static Mixer.

System	Temperature	$\eta_r(\text{PE})$ $\eta_r(\text{PS})$	Dimension	Composition (PE/PS)				
				90/10	70/30	50/50	30/70	10/90
PE-1/PS	180°	3.1	d_n	1.0	1.0	1.75	1.5	0.5
			d_w	1.1	1.25	2.25	1.8	0.8
PE-2/PS	180°	1.6	d_n	2.4	3.4	5.8	2.0	1.2
			d_w	2.9	3.9	9.15	2.6	1.45
	240°	3.8	d_n	2.2	3.2	3.7	3.4	1.8
			d_w	3.0	3.6	4.4	5.4	2.6
PE-3/PS	180°	0.13	d_n	1.1	2.0	2.7	4.7	0.4
			d_w	1.55	2.0	3.25	6.9	0.5

Table 4. Dimensions of Discrete Phase of PE-2/PS PE-2/N6 and PE-2/PC Blends at 240°C.

System	$\eta_r(\text{PE-2})$ η_r	Dimension (μm)	Composition (PE-2/—)				
			90/10	70/30	50/50	30/70	10/90
PE-2/PS	38	d_n	2.2	3.2	3.7	3.4	1.8
		d_w	3.0	3.6	4.4	5.4	2.6
PE-2/N6	67	d_n	3.8	5.0	24.9	11.6	10.3
		d_w	5.2	5.7	33.4	14.0	13.3
PE-2/PC	6.3	d_n	2.4	2.6	12.8	8.8	—
		d_w	2.7	3.1	18.0	10.3	—

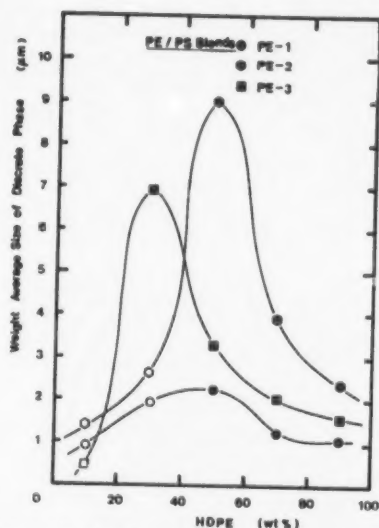


Fig. 5. Dispersed-phase dimensions of PE-1/PS, PE-2/PS, and PE-3/PS blends from static mixer at 180°C.

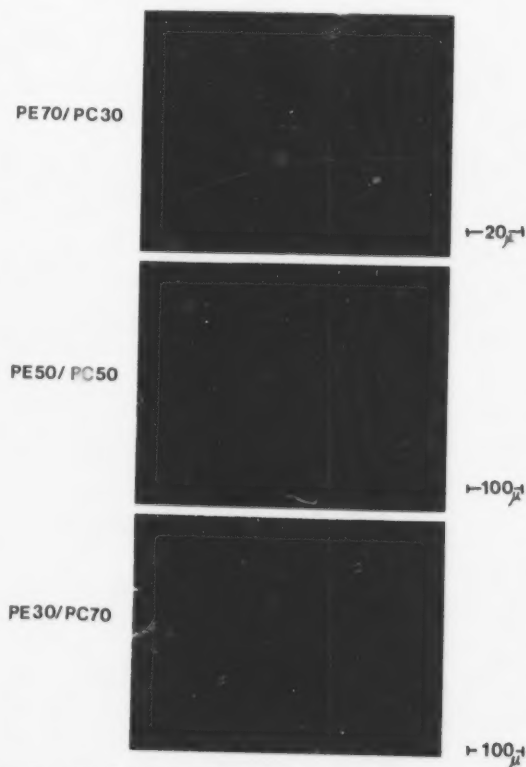


Fig. 6a. SEM photomicrographs of cross-sectional phase morphology of PE-2/PC blend as a function of composition 70/30, 50/50, and 30/70.

for the PE-2/N6 blends. The finest morphologies are developed in the PE/PS system.

We have also investigated the longitudinal cross sections of the extrudates, particularly the PE/PS systems. These are summarized in Figs. 10 to 12. The PE-3/PS—10/90 form long thin fibrils while the 90/10 forms spherical droplets. The PE-2/PS—

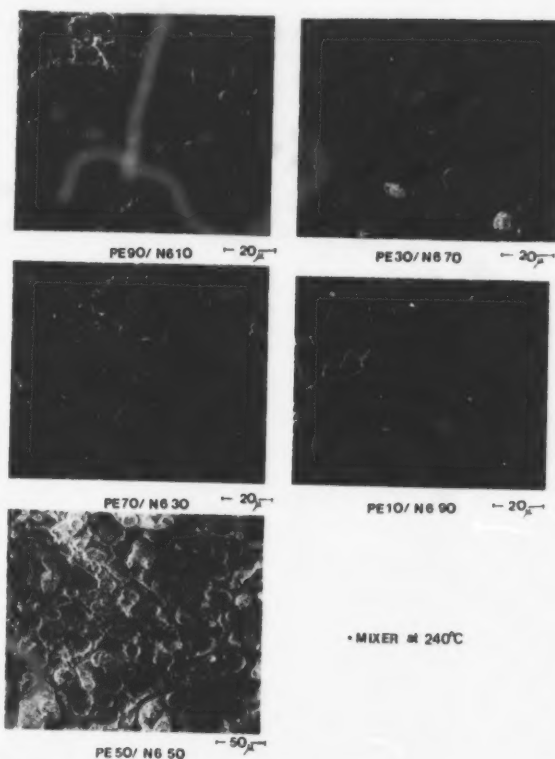


Fig. 6b. SEM photomicrographs of cross-sectional phase morphology of PE-2/N6 blend as a function of composition, 90/10, 70/30, 50/50, 30/70, and 10/90.

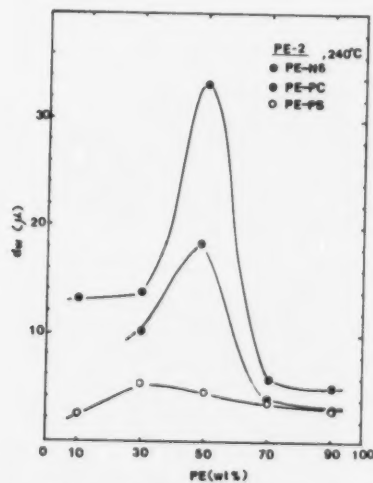


Fig. 7. Dispersed-phase dimensions of PE-2/PS, PE-2/N6, and PE-2/PS blends from static mixer at 240°C.

90/10 and 10/90 form long thin fibrils and dispersed-phase droplets, respectively. the PE-1/PS—90/10 and 10/90 both exhibit long thin threads which undulate in diameter.

DISCUSSION

Phase Morphology Transverse to Flow

First we consider blends from the static mixer.

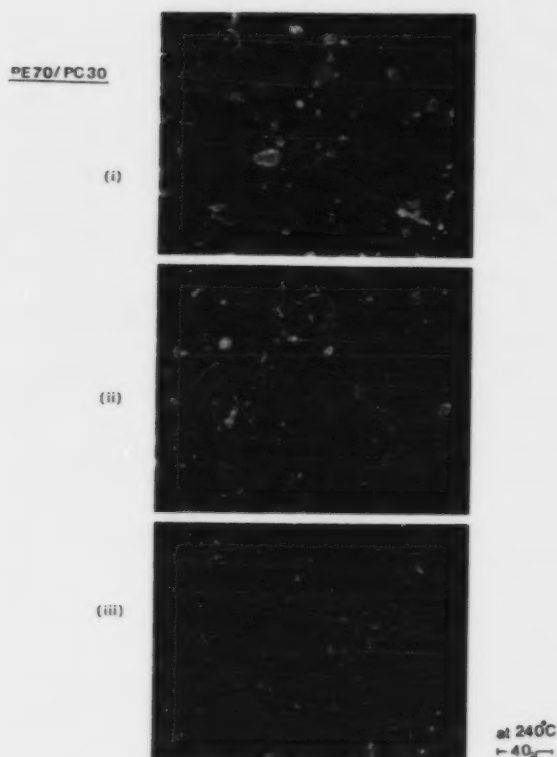


Fig. 8a. SEM photomicrographs of PE-2/PC-70/30 blends as a function of die-wall shear stress (i) 9.6×10^4 (ii) 2.3×10^5 (iii) 5.5×10^5 dyne/cm².

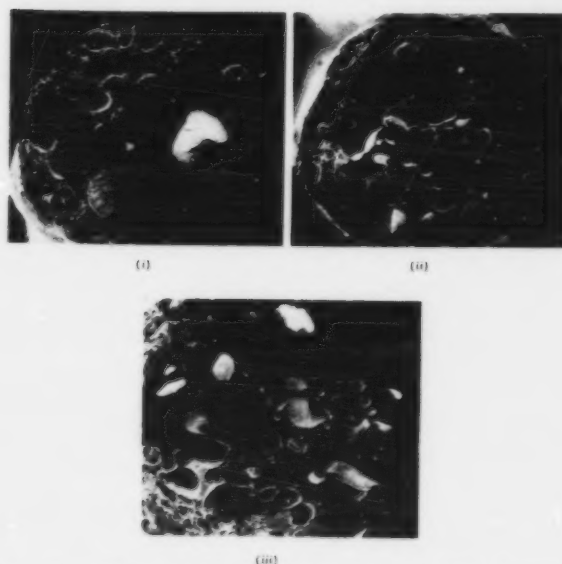


Fig. 8b. SEM photomicrographs of PE-2/N6-50/50 blends as a function of die-wall shear stress (i) 2.5×10^4 (ii) 8.3×10^4 (iii) 2.2×10^5 dyne/cm².

The PE-2/N6 blends, when N6 is the continuous phase, have the coarsest dispersions and the PE-2/PS systems as a whole have the finest morphologies. The PE/PS results are similar to those reported by other investigators of the polyethylene/polystyrene

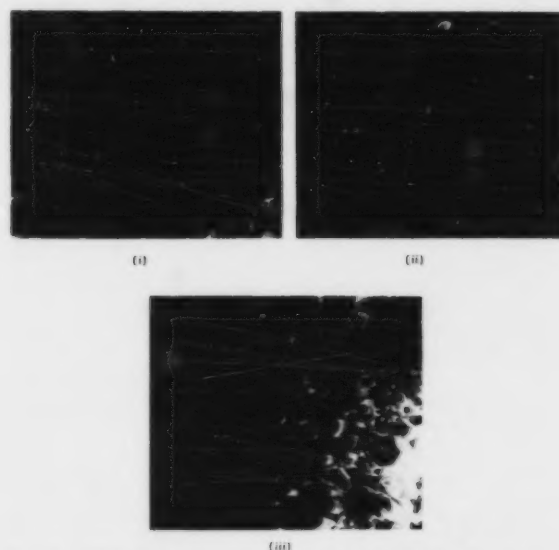


Fig. 8c. SEM photomicrographs of PE-2/PC-50/50 blends as a function of die-wall shear stress (i) 1.0×10^5 (ii) 2.6×10^5 (iii) 6.2×10^5 .

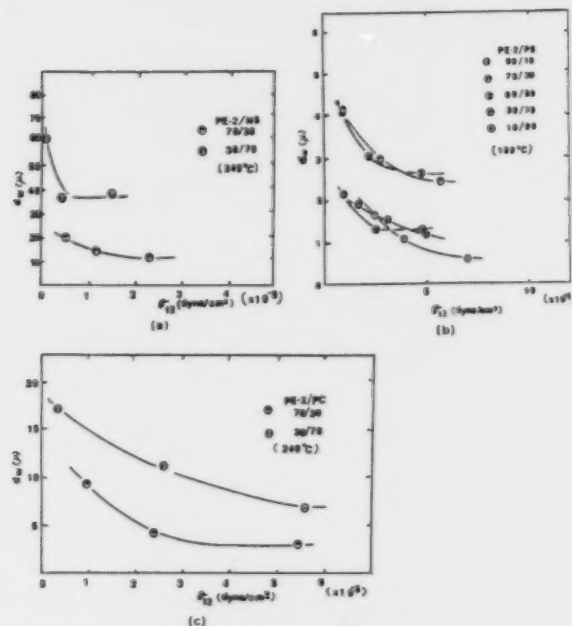


Fig. 9. Dispersed-phase dimensions of (a) PE-2/N6, (b) PE-2/PS, (c) PE-2/PC, 70/30 and 30/70 blends as a function of die wall shear stress.

system (11, 14, 15). A coarser blend morphology of polypropylene and nylon-6 has been noted by Liang, *et al.* (10) who also observed the existence of phase growth in quiescent systems.

It seems clear that the primary factors determining blend morphology in these systems are the differences in polarity between the phases and the viscosity of the continuous phase. This may be interpreted in terms of the relative importance of interfacial and viscous forces. The interfacial forces are κ/L where κ is the interfacial tension and L , a

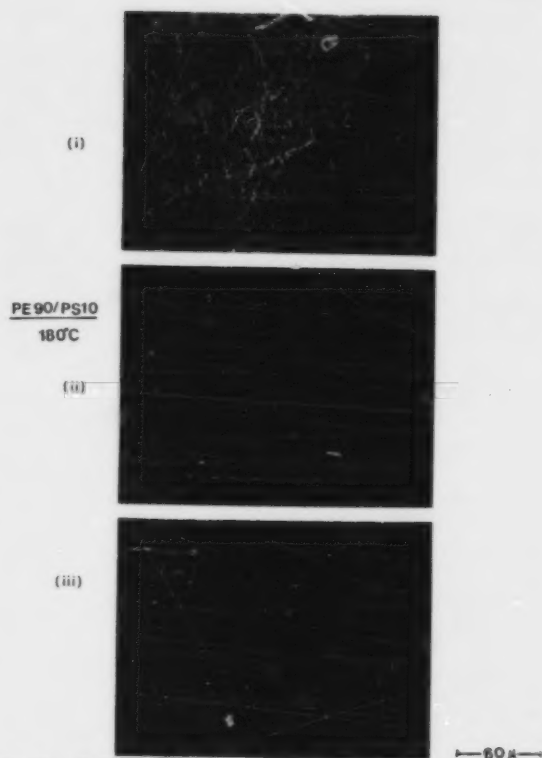


Fig. 10a. SEM photomicrographs of longitudinal cross section of extrudates of PE-2/PS-90/10 blends as a function of viscosity ratio η_d/η_m (i) 1.7 (ii) 1.5 (iii) 1.4.

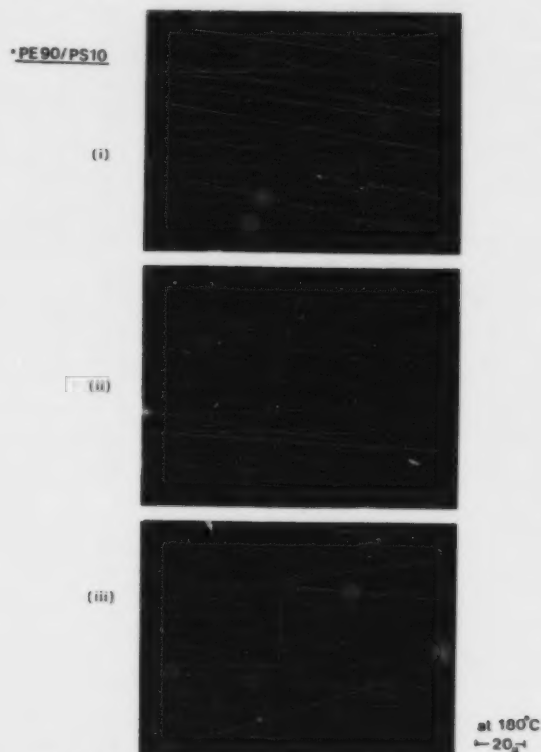


Fig. 11a. SEM photomicrographs of longitudinal cross sections of extrudates of PE-1/PS blends-90/10 as a function of viscosity ratio η_d/η_m (i) 0.8 (ii) 0.9 (iii) 0.8.

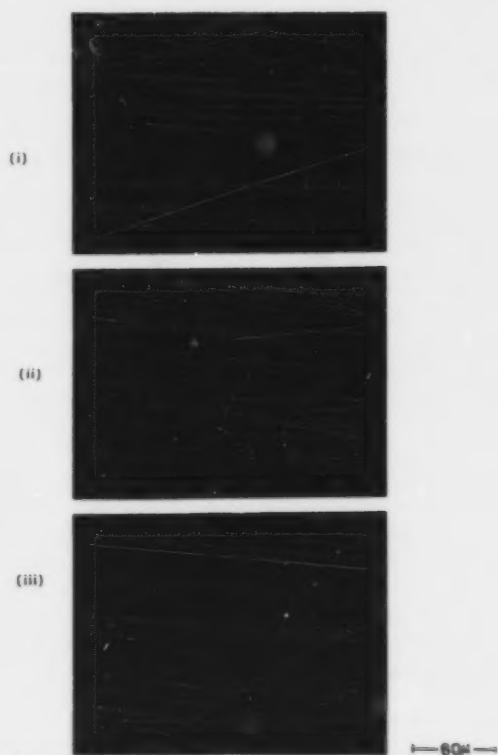


Fig. 10b. SEM photomicrographs of longitudinal cross sections of extrudates of PE-2/PS-10/90 blends as a function of viscosity ratio η_d/η_m (i) 0.5 (ii) 0.7 (iii) 0.7.

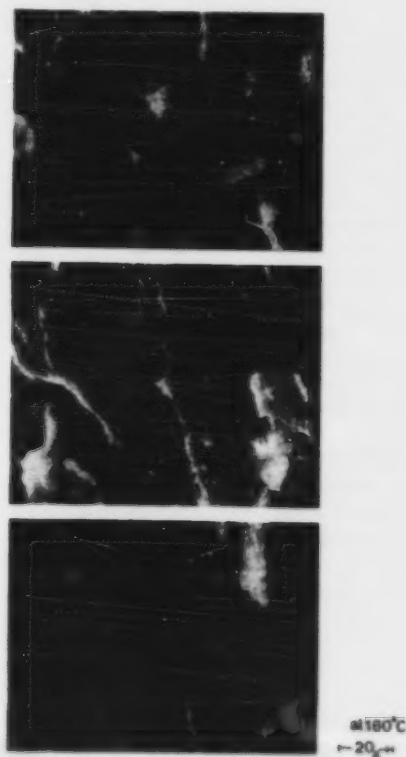


Fig. 11b. SEM photomicrographs of longitudinal cross section of extrudates of PE-1/PS-10/90 blend as a function of viscosity ratio η_d/η_m (i) 0.8 (ii) 0.6 (iii) 0.4.

PE90/PS10

(i)



(ii)



(iii)

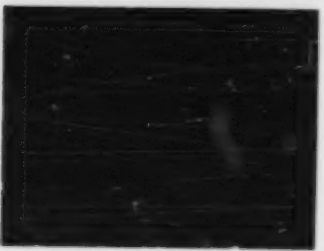
at 180°C
40μm

Fig. 12a. SEM photomicrographs of longitudinal cross sections of extrudates of PE-3/PS 90/10 blend as a function of viscosity ratio η_d/η_m (i) 2.2 (ii) 2.7 (iii) 3.7.

characteristic length. The viscous forces have the form $\eta V/L$ where η is the viscosity, V is a characteristic velocity, and L a characteristic length. The ratio of these is

$$\frac{\kappa/L}{\eta V/L} = \frac{\kappa}{\eta V} = \frac{\kappa}{\eta \dot{\gamma} R} \quad (2)$$

where $\dot{\gamma}$ is a shear rate and R a dimension representative of the scale of the blend morphology. If this group has similar values in different systems, then large R is associated with large κ , small η and small $\dot{\gamma}$. If the differences in polarity are

nylon-6 > polycarbonate > polystyrene

relative to polyethylene, this agrees with experiment. The problem is that there is a lack of reliable experimental data for evaluating κ .

The decrease in scale of the dispersed-phase morphology with capillary die extrusion rate has been noted by various earlier investigators. Quite strong effects have been described by Liang, *et al* (10). Similar but less striking behavior has been noted by Min, *et al* (11). The phase growth of polypropylene (PP)/nylon-6 has been reported by Liang, *et al* (10). Similar results for polyethylene (PE-2)/nylon-6 and polyethylene (PE-2)/polycarbonate (PC) have been observed in Fig. 8b and c. Attention is called to the material in the center of the cross sections of PE-2/N6—50/50 and PE-2/PC—50/50. An increase in phase dimensions compared with the extrudates

PE10/PS90

(i)



(ii)



(iii)

at 180°C
40μm

Fig. 12b. SEM photomicrographs of longitudinal cross sections of extrudates of PE-3/PS 10/90 blend as a function of viscosity ratio η_d/η_m (i) 0.5 (ii) 0.4 (iii) 0.3.

from the static mixer is clear. For the series of polyethylene-polystyrene blends, the decrease of dispersed-phase dimension was explored by varying viscosities of both PE and PS. Little change was found. It would appear that the coarseness of the morphology depends primarily upon the interfacial tension.

As noted above, we observe that the phase dimensions decrease with increasing shear rate, $\dot{\gamma}$, or shear stress, $(\sigma_{12})_w$. The data may be correlated using the dimensionless group of Eq 2 if we arbitrarily choose values for the interfacial tension. Taking κ for PE/PS to be 0.8, PE/PC to be 15, and PE/N6 to be 30 dyne/cm, we obtain the plot shown in Fig. 14. A good correlation is obtained.

Longitudinal Phase Morphology

Droplet-to-fiber in Newtonian fluids has been studied by various investigators (16–20). Two dimensionless parameters $\kappa/\eta V$ and η_d/η_m (dispersed/matrix) were discussed for the droplet-to-fiber transition. They note that the major parameter for fiber formation was the viscosity ratio η_d/η_m of the dispersed fluid to the medium. They reported that if the viscosity ratio was close to unity, a uniform thin-thread fibril was formed. The longitudinal morphologies of the PE/PS blends are summarized in Table 5. The viscosity ratios of η_d/η_m recalculated for the appropriate shear stresses at 180°C are included in this table. Uniform filamentous mor-

Table 5. Longitudinal Phase Morphology of Polyethylene/Polystyrene Blends.

PE/PS Composition	Fibrillation	η_d/η_m (dispersed/matrix)	d_w (μm)
PE-1/PS			
10/90	undulating thread	1.2-1.3	0.4-0.8
90/10	undulating thread	0.8-1.3	0.7-1.8
PE-2/PS			
10/90	thin thread	0.5-0.7	0.5-1.7
90/10	ellipsoids	1.4-1.7	1.3-2.1
PE-3/PS			
10/90	thin thread	0.3-0.5	0.3-1.3
90/10	spheres	2.2-3.7	6.5-6.9

phologies occur when η_d/η_m is from 0.3 to about 1.0. Dispersed droplets are formed when η_d/η_m is greater than 2.2. It can be concluded that when the dispersed phase has less viscosity than the continuous phase, the droplets are elongated by the shear stress and form fibrils parallel to the flow direction as shown in Fig. 13. When this dispersed phase has a very high viscosity, it is not possible to deform the suspended droplets except with very large stresses.

Effect of Viscoelastic Behavior

Van Oene (21) has argued that incompatible blend morphology is determined by viscoelastic, specifically normal stress characteristics as the interfacial tension is influenced by the elastic energy in the two phases. We do not see any direct evidence of this in our studies. Figure 2 indicates a wide range of N_1 - σ_{12} relationships for the different polymer melts investigated. The ordering for these materials does not obviously correlate with the coarseness of the phase morphology or droplet-fibril transitions for the blend systems. The only correlation seems to be with differences in chemical composition and viscosity ratio. The greater the differences in polarity, the greater the scale of phase dimensions. Fibrillar morphologies result from lower or equal viscosity disperse phases. However, the values of interfacial tension for PE/N6 and PE/PC which are needed to develop a general correlation are much larger than would be expected. It could be that these large values are the results of normal stress differences in addition to quiescent interfacial tensions.

CONCLUSIONS

A study of the development of phase morphology during processing of various systems of high-density polyethylene/polystyrene (PE/PS) blends, high-density polyethylene/Nylon 6 (PE/N6), and high-density polyethylene/polycarbonate (PE/PC) blends has been reported. Certain trends are clear.

- The phase morphologies of PE/PS blends developed by a screw-extruder/static-mixer system generally involve phase dimensions of 1-5 μm except at near 50/50 loadings when dimensions up to 10 μm are obtained. This is true for widely varying viscosity ratios, temperatures and molecular weights. Some reduction is obtained by sub-

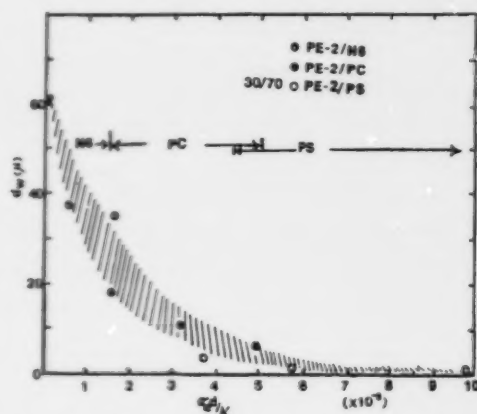


Fig. 13. Plots of dispersed-phase dimensions of PE-2/PS, PE-2/PC, and PE-2/N6-30/70 blends as a function of dimensionless term ($\sigma_{12} d/\kappa$).

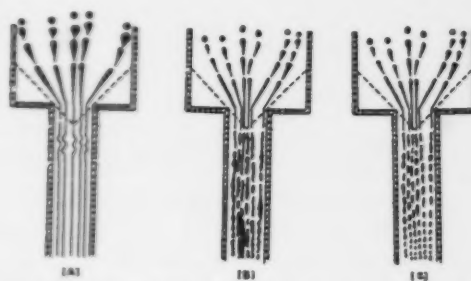


Fig. 14. The schematic view of longitudinal phase morphologies at various viscosity ratios $\eta_d/\eta_m = \lambda$.

- (A) $\lambda < 0.7$
- (B) $0.7 < \lambda < 1.7$
- (C) $\lambda > 2.2$.

sequent shearing in viscometric instruments. Phase dimensions as fine as 0.6 are obtained in a 10/90 PE/PS at higher shear rates in a capillary die.

- The phase morphologies of PE-2/N6 and PE-2/PC systems developed by a screw extruder/static mixer system are much coarser than those of PE/PS systems in co-continuous morphologies and when PE is the continuous phase. The order of coarseness is: N6 > PC > PS. In studies of capillary die flow, we found that with increasing shear stress, this dispersed phase becomes finer in the outer layer of the extrudate but remains coarser near the center line. This phenomenon would appear to be due to the higher interfacial tension. In these systems this is coupled with the fact that high stress occurs only in the outer regions of the capillary. Correlations are developed between dispersed phase and the dimensionless group $\kappa/\eta\gamma R$.
- The longitudinal morphology of polyethylene/polystyrene blend extrudates was found to be influenced by the viscosity ratio η_d/η_m . If this is less than $0.7 < \eta_d/\eta_m < 1.7$, the droplets became undulant fibers or rods. If $\eta_d/\eta_m > 2.2$, undeformed droplets are observed.

ACKNOWLEDGMENT

This research was supported by the Polymers Section of The Division of Materials of The National Science Foundation, through Grant No. DMR 8026051.

REFERENCES

1. M. V. Tsebrenko, M. Jakob, M. Yu Kuchinika, A. V. Yudin, and G. V. Vinogradov, *Int. J. Polym. Mater.* **3**, 99 (1974).
2. C. D. Han, Y. W. Kim, and S. J. Chen, *J. Appl. Polym. Sci.* **19**, 2831 (1975).
3. M. V. Tsebrenko, A. V. Yudin, T. I. Ablazova, and G. V. Vinogradov, *Polymer* **17**, 831 (1976).
4. G. N. Avgeropoulos, F. C. Weissert, P. H. Biddison, and G. A. Bohm, *Rubber Chem. Technol.*, **49**, 93 (1976).
5. C. J. Nelson, G. N. Avgeropoulos, F. C. Weissert, and G. A. Bohm, *Ang. Makromol. Chem.*, **60-61**, 49 (1977).
6. S. Danesi and R. S. Porter, *Polymer*, **19**, 448 (1978).
7. N. Alle and J. Lyncaae-Jorgenson, *Rheol. Acta*, **19**, 104 (1980).
8. M. V. Tsebrenko, N. M. Rezanova, and G. V. Vinogradov, *Polym. Eng. Sci.*, **20**, 1023 (1980).
9. J. Shimizu, N. Okui, T. Yamamoto, M. Ishii, and A. Takaku, *Seni-Gakkaishi*, **38**, T-1 (1982).
10. B. Liang, J. L. White, J. E. Spruiell, and B. C. Goswami, *J. Appl. Polym. Sci.*, **28**, 2011 (1983).
11. K. Min, J. L. White, and J. F. Fellers, *J. Appl. Polym. Sci.* **29**, 2117 (1984).
12. C. D. Han, "Rheology in Polymer Processing", Academic Press, NY (1976).
13. K. Oda, J. L. White, and E. S. Clark, *Polym. Eng. Sci.*, **18**, 25 (1978).
14. W. M. Barentsen and D. Heikens, *Polymer*, **14**, 579 (1973).
15. C. D. Han and Y. W. Kim, *Trans. Soc. Rheology*, **19**, 245 (1975).
16. G. I. Taylor, *Proc. Roy. Soc. London*, **A138**, 41 (1932), **A146**, 501 (1934).
17. H. Karam and J. C. Bellinger, *Ind. Eng. Chem. Fundam.*, **7**, 576 (1968).
18. F. D. Rumscheidt and S. G. Mason, *J. Colloid Sci.*, **16**, 238 (1961).
19. S. Torza, R. Cox, and S. G. Mason, *J. Colloid Sci.*, **38**, 395 (1972).
20. S. Tomotika, *Proc. Roy. Soc.*, **A150**, 322 (1935).
21. H. Van Oene, *J. Colloid Interf. Sci.* **40**, 440 (1972) and in "Polymer Blends," edited by D. R. Paul and S. Newman, Academic Press, NY (1978).

DISCUSSION

L. A. Utracki: I am surprised that you are using the steady-state rotational method to study the flow properties of these multiphase systems. In our own work, as well as in the literature, there are numer-

ous observations of phenomena related to change of the sample structure in this type of deformation: shear segregation, coalescence, fractionation, etc. This was the main reason why we adopted low-strain dynamic testing as the universal method of study of the multiphase systems; the sample morphology was found to be unaffected by such testing. By contrast, the steady-state rotation in most cases generated a "tree ring" morphology; i.e. the sample structure changed with shear. Is this what you want? If so, how can you correlate the rheology with the sample structure? On a similar subject—the use of a motionless mixer for blending. There are reports indicating that motionless mixers may cause demixing of polymer blends, i.e. with increase in the number of mixing elements the morphology coarsens. Could you please tell us why you selected the motionless mixer? What are the advantages? Are you satisfied that this is an optimal method for generating reproducible blend structures of your systems? Did you examine the other mixers?

K. Min: We did not observe any evolution of phase morphology in the steady-state flow of our blends in capillary dies. The phase morphologies were not and did not tend to become the "onion skin" type. We observed skin-core structures only in the products of our screw extrusion without the static mixing elements in place. Dispersion was always improved by the introduction of static mixing elements. Micron-level dispersion was obtained.

G. Vexler: I would like to ask you how the entrance to the die was designed. The entrance vortex effects can have profound influence on the blend morphology.

K. Min: We used both 180° and tapered-entrance dies in our experiments. No changes in phase morphology were observed.

G. Vexler: I expected that for systems with high interfacial difference you could have more coalescence at the entrance due to vortex effect. This should be particularly easy to observe in nylon blends where you have nearly Newtonian liquid mixed with a non-Newtonian one.

K. Min: We have no knowledge of flow patterns at the die entrance for our blend systems. It is known that polystyrene exhibits die-entrance vortices. It is not apparent how to interpret our results in terms of such a hypothesis.

Permeability of Oxygen and Water Vapor Through Polyethylene/Polyamide Films

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Oxygen and water vapor permeability studies were carried out on binary polyethylene/polyamide immiscible blends incorporating three polyethylene resins (LDPE, LLDPE, and HDPE), and three polyamide resins (PA-6, PA-6,6, and modified PA-6,6m). It was found that the incorporation of PA into PE reduces the oxygen permeability while water vapor permeability is increased. In the range of 0 to 30 weight percent of PA, the oxygen permeability of PE was reduced by a factor of 2.8 to 3.6. Maximum water vapor permeabilities increased: for HDPE by a factor of about 2.6 to 3.1 and for LDPE and LLDPE blends by about 1.6.

INTRODUCTION

The demand for packaging materials to be used for foodstuffs is ever on the increase (1). Generally, packing materials should possess low permeability to oxygen, water vapor, carbon dioxide, aromatic substances, and the like (2 to 8). Polymers, and products made from polymers, have captured a large portion of the packaging materials industry. The main attraction is their low cost, flexibility, and desirable mechanical and thermal properties. However, the permeability of polymeric materials to gases and vapors is not always satisfactory.

The term "barrier plastics" is applied to several groups of plastics which have very low permeability to gases and/or water vapor (5). Different techniques have been developed to produce such material (2, 9 to 11). These techniques are: layering of polymers with different barrier properties by coextrusion lamination or coating, as well as metalization, orientation, *e.g.* biaxial stretching, addition of solids, *viz.* mica, and blending. The latter method will be discussed in the following text.

The principal aim of this study is to evaluate the feasibility of producing polyethylene/polyamide blends having good oxygen and moisture barrier properties.

DIFFUSION THROUGH MULTIPHASE POLYMERS

Permeation through polymer films is a result of two distinct processes: solubility, which is a ther-

modynamic quantity, and diffusion, a kinetic one (12 to 17):

$$P = DS \quad (1)$$

where P , D , and S are the permeability, diffusion, and solubility coefficients, respectively.

Factors influencing permeability through a polymeric film can be divided into: external (temperature, T , pressure, concentration, c , humidity, RH , etc.); due to penetrant (solubility, molecular shape, weight, etc.); and due to polymer (14 to 22). It is recognized (23) that during the permeation the structure of the polymer changes. In the presence of penetrant molecules a partial plasticization, *i.e.* enhancement of chain mobility, may take place to lead to stress relaxation, shrinkage, phase ripening, etc.

The simplest multiphase material is a semicrystalline polymer. It has been shown that the sorption and diffusion coefficients in the crystalline phase are substantially smaller than in the glassy or rubbery phases. As a result, it is generally assumed (24 to 29) that the crystalline phase does not sorb, and hence, does not allow any penetrant to diffuse through it. In this case D depends on the volume fraction of the amorphous phase, α , the tortuosity of penetrant path, τ , and the "blocking factor", B_1 :

$$D = D_a \alpha n / B_1 \tau, \quad (2)$$

where D_a is the diffusion coefficient in a hypothetical, completely amorphous polymer, and $n \approx 1$ is an empirical parameter, dependent on the nature

of the penetrant molecule. In principle, Eq 2 can be used to interpret data of any multiphase system writing B_1 and τ as functions of concentration and process variables (30, 31). In polymer blends the dispersed phase could be incorporated in a wide range of volume fractions, particle sizes, and particle shapes, distributed randomly or in an orderly fashion. For blends containing a permeable matrix with a nonpermeable dispersed (uniform spheres) phase, the Maxwell tortuosity equation (32) may be used:

$$\tau = (3 - \alpha)/2 \quad (3)$$

Relaxing the condition of nonpermeability (33), the following relation for spherical and cylindrical dispersions has been proposed:

$$\tilde{p} = 1 + (f + 1)(\tilde{p}_2 - 1)c / [(\tilde{p}_2 + f) - (\tilde{p}_2 - 1)c], \quad (4)$$

where: $\tilde{p} = P/P_1$, $\tilde{p}_2 = P_2/P_1$, $c = 1 - \alpha$ and the subscripts 1 and 2 refer to the continuous and dispersed phase, respectively. The shape factor $f = 1$ gives the Rayleigh relation for cylinders, while $f = 2$ yields the Maxwell relation for spheres. Models of permeation through series of laminates (34) give:

Series laminate:

$$\tilde{p} = 1/\alpha + \tilde{p}_2/c \quad (5)$$

Parallel laminate:

$$\tilde{p} = \alpha + \tilde{p}_2 c \quad (6)$$

Recently, more complex morphologies have also been analyzed (35, 36). The dispersed phase consisted of regularly arranged rectangular parallelepipeds. Since the morphology of blends is influenced by processing conditions, composition, and thermodynamics, this treatment may eventually lead to the use of P as a means to generate structural information. Small molecules, *viz* He, H₂, do not interact with polymers, hence they do not alter blend morphology and may be used as structural probes.

The most extensive experimental data pertaining to permeability in polymer blends are those of Ranby and Shur (37, 38). These data have been analyzed qualitatively in terms of limiting models and have been interpreted in terms of the semi-log plot of permeability versus blend composition. Suggestions of immiscibility consequent to the observation of S-shaped semi-log permeability composition plots are supported by dynamic mechanical and/or X-ray diffraction and density studies of the blends.

Robeson and coworkers (39) have also analyzed permeation data, but their focus is based upon detailed and quantitative interpretation of data in terms of composition of component phases. Peterson's data (33) on oxygen permeability through various blends have been compared with the Higuchi model. The experimental data compare well with this model. Masi, *et al* (40) studied CO₂ diffu-

sion through copolyester/polycarbonate blends. Odani, *et al* (41) measured D , S , and P for gases in styrene-butadiene-styrene block polymers. Recently Barrie, *et al* (42) reported transport properties of hydrocarbon vapors through block and graft poly(dimethyl siloxane-co-styrene) and blends of poly(dimethyl siloxane) with EPR.

Data relating to oxygen permeability through polyethylene/polyamide-6 are scarce (43), whereas those for polyethylene/polyamide-6/water, polyethylene/polyamide-6,6/oxygen, and polyethylene/polyamide-6,6/water have not been reported. However, studies of permeability of gases and water vapor through the pure polymers (21, 33, 44, 45) have been published.

EXPERIMENTAL

Polyethylene and Polyamide Base Resins

Binary blends have been prepared utilizing three polyethylenes and three polyamides. Tables 1 and 2 provide the characteristics of these resins, respectively.

Blend Compositions

Each of the polyethylenes was blended separately with PA-6 and PA-6,6, whereas the PA-6,6m was only blended with HDPE. For each combination six different blend compositions were prepared (0, 10,

Table 1. Characteristics of Polyethylene Resins.⁽¹⁾

Property	Low-Density Polyethylene	Linear-Low-Density Polyethylene	High-Density Polyethylene
Code	LDPE	LLDPE	HDPE
Density kg/m ³	924	918	961
Melting Point (°C)	113	116	134
Melt Index (gm/10 min)	0.8	1.0	0.72
Thermal Conductivity	8.3 × 10 ⁻⁴	—	11–12 × 10 ⁻⁴
Specific Heat ⁽³⁾	2.3	—	1.85
M_n	34,500	35,000	15,700
M_w	—	115,000	107,600
M_z	—	283,000	370,000

⁽¹⁾ Source: Union Carbide

⁽²⁾ Units in cal/cm s °C

⁽³⁾ Units in KJ/kg K at 25°C

Table 2. Characteristics of Polyamide Resins.⁽¹⁾

Property	Polyamide 6	Polyamide 6,6	Elastomer Modified Polyamide 6,6
Code	PA-6	PA-6,6	PA-6,6m
Density kg/m ³	1130	1140	1080
Melting Range (°C)	210–228	255–270	255
Thermal Conductivity	—	0.25 ⁽²⁾	—
Specific Heat	0.4	0.4	—

⁽¹⁾ Source: DuPont

⁽²⁾ Units in W/m K

15, 20, 25, and 30 weight percent polyamide) with the exception of the blends containing PA-6,6 and LDPE, for which in addition a 5 percent sample was also prepared. In all, 43 samples were made.

Conditioning of Resins and Blends

The hydrolyzing and plasticizing effects of water in polyamides is well known. For this reason, before blending all PA-resins were dried at 85°C and 100 kPa for 72 h, while the PE-resins were dried at the same conditions for 24 h. The blend films were similarly dried for 22 to 24 h prior to conditioning in the permeability apparatus.

Preparation of Blends

Blends were prepared using the C.W. Brabender Plasticorder, $\frac{3}{4}$ -inch single screw extruder, with right pitch screw with a length to diameter ratio of 25, slit die ($h = 0.8$ mm) and four-roll calendaring take-out system. Temperature control was achieved by means of three electric heaters along the barrel and one heater at the die. Compressed air cooling was employed when necessary. Screens of 80 and 100 mesh were placed between the pumping zone and the die to provide for better mixing. In the case of PA-6,6 blends with the T in the three zones were: 270, 280, and 290 with 300°C at the die, and that of PA-6 blends 220, 230, 240, and 250°C, respectively. The screw speed was 30 rpm. The initial 1.5 kg of the extrudate were discarded in order to ensure steady-state operation and to flush impurities out of the system before collecting blend samples.

Preparation of Films and Resins and Blends

Films were prepared by compression molding between Mylar sheets, as in similar studies (43, 27 to 29, 38). The temperature of the platens was set at 275°C for PA-6,6 and 230°C for PA-6 blends; PE resins were molded at 140 to 155°C. A force of 25 t was applied. Eight films were prepared for each batch with the average thickness of 50 to 75 μ m and thickness variation ± 2.5 μ m.

Permeation of Oxygen Through Blend Films

ASTM D 3985 - 81 method was used with the Ox-Tran 100 Twin Model from Modern Controls Inc., Minnesota.

Permeation of Water Vapor Through Blend Films

ASTM test F 372 - 73(78) was performed using Permatran W, manufactured by Modern Controls Inc., Minnesota.

Scanning Electron Microscopy (SEM)

Films of the blends were fractured in two halves at liquid nitrogen temperatures. To dissolve the polyamide, one part of each film was placed in formic acid for about 24 hours, then taken out, washed with demineralized water and dried. Both acid-treated and untreated parts were observed under SEM-JEOL Model JSM-35CF.

Fourier Transform Infrared Spectroscopy (FTIR)

The composition of blends was determined by FTIR, using Nicolet 170SX instrument equipped with mercury cadmium telluride detector and supplied by Nicolet software. For quantitative analysis the calibrating PE and PA sample thickness was calculated from interference fringes. The blend composition was determined comparing the integrated areas under the following bands:

Band 1: 1322 - 1230 cm^{-1} (due mainly to polyamide).

Band 2: 740 - 710 cm^{-1} (due mainly to polyethylene).

The error analysis indicated maximum error to be below 2 percent. The results confirmed the compositions expected from the weighed-in quantities of the neat resins; viz. FTIR results: 20, 23, 22, 16, 9, 16, and 17 weight percent of PA while expected compositions were respectively: 20, 25, 20, 15, 10, 15, and 20 weight percent of PA. In the following calculations the "expected" values were used.

RESULTS

Permeability of the Neat Polymers

A comparison of oxygen and water vapor permeabilities obtained from the literature and those measured in the present work are shown in Table 3. Except for O_2 permeability of HDPE a good agreement was found. However, the value quoted for this resin in (44) seems to be rather high; $P = 533 \times 10^{-16}$ was reported by Matzner *et al* (43).

Blend Permeability

The results for O_2 permeability are reported in Figs. 1 and 2 and those for H_2O in Figs. 3 and 4. In all cases the average value of P measured for 4 samples is plotted as a function of volume percent of PA. The lines were drawn only to indicate the trend. The standard deviation of measurements varied from 0.4 to 4.1 percent (see also Table 4).

Microstructure of the Blends

Both microstructure and blend composition have a strong influence on permeability behaviour (35,

Table 3. Experimental and Reported Oxygen/Water Vapor Permeabilities of Neat Resins.

Resin ⁽³⁾	Oxygen ⁽¹⁾ Permeability $\times 10^{16}$		Water Vapor ⁽²⁾ Permeability $\times 10^{11}$	
	Experimental	Literature Values	Experimental	Literature Values
LDPE ⁽⁴⁾	2082	1958	4.37	4.56
HDPE ⁽⁴⁾	625	832	1.37	1.37
LLDPE	1920	—	4.06	—
PA-6 ⁽⁴⁾	11.7	11.7	87.6	86.4
PA-6,6 ⁽⁵⁾	9.08	8.99 ⁽⁴⁾	91.2	91.2 ⁽⁵⁾
PA-6,6m	20.9	—	39.7	—

Notes: (1) Units in $\text{cm}^3 \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$; Temperature: 25°C; relative humidity: 0 percent.
 (2) Units in $\text{gm} \cdot \text{cm}/(\text{cm}^2 \cdot \text{s})$; Temperature: 37.8°C; relative humidity: 90 percent.
 (3) Reference number indicating source of literature values.
 (4) At 23°C and 50 percent R.H.
 (5) At 23°C and 100 percent R.H.

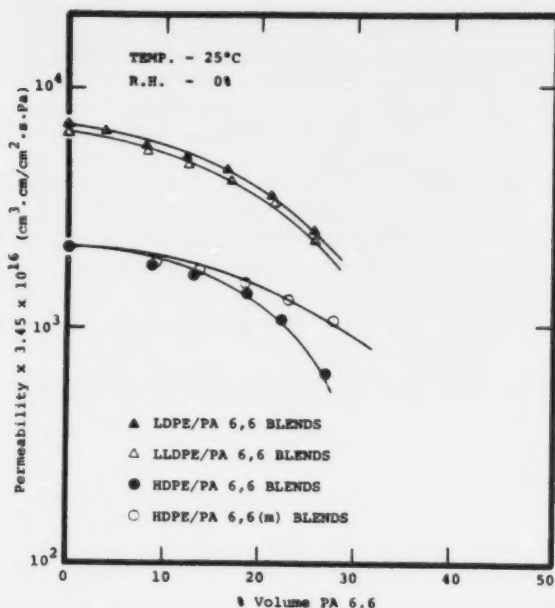


Fig. 1. Oxygen permeability vs PA-6,6 content for its blends with PE's; experimental results.

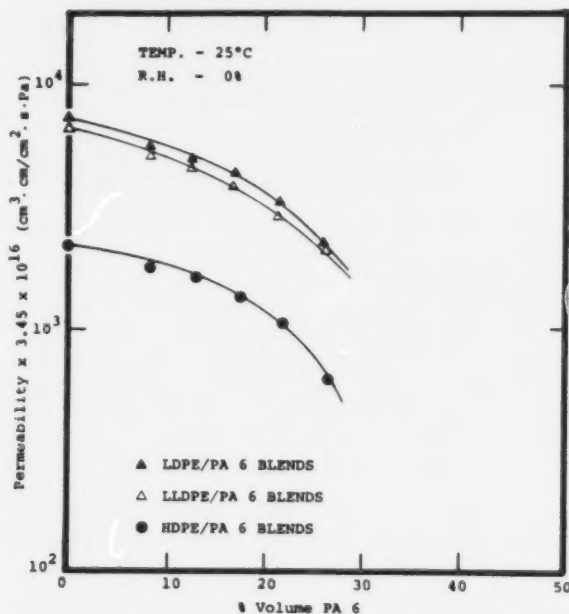


Fig. 2. Oxygen permeability vs PA-6 content for its blends with PE's; experimental results.

36, 43, 45 to 48). All the prepared blends were translucent. Moreover, when films prepared from the blends were folded, phase separation was observed in the form of stress whitening. These observations suggested that the blends incorporated two immiscible phases (47, 49 to 51). The SEM was employed not only to examine the boundaries between phases, but also to observe the size, shape, and orientation distribution of the dispersed phase in the continuous matrix. Fractured (untreated and acid-treated) film surfaces were observed under the

scanning electron microscope. In the following micrographs (Figs. 5 to 10) A denotes the part not treated with formic acid, whereas B refers to the corresponding treated one. All the samples contained 20 weight percent of PA in PE. The micrographs show that in all blends PA is randomly dispersed in the form of spheres of 0.1 to 5 μm diameter and larger cylindrical bodies. The SEM's of the samples containing both lower and higher concentration of PA indicated either only spheres (at 10

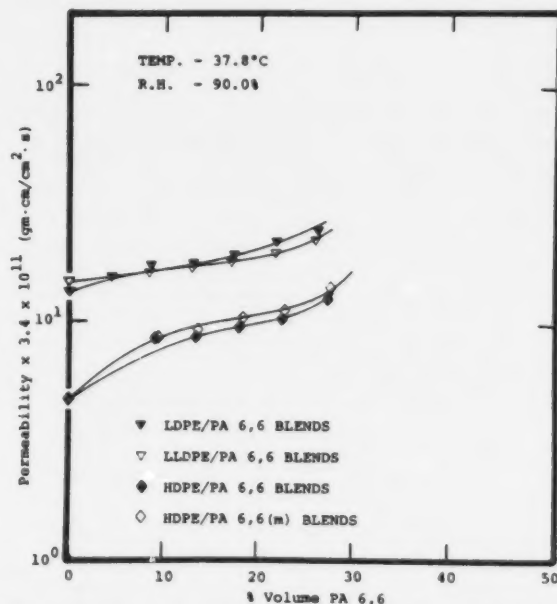


Fig. 3. Water vapor permeability versus PA-6,6 content for its blends with PE's; experimental results.

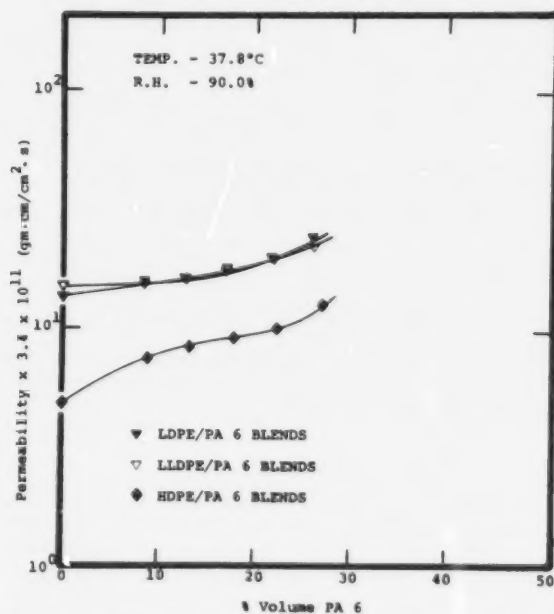


Fig. 4. Water vapor permeability versus PA-6 content for its blends with PE's; experimental results.

Table 4. Effect of Addition of 30 Weight Percent of PA on PE-Permeability.

No.	Resins		Permeability		100 × P/P ₁ (st. dev.)	
	Pe	Pa	Oxygen ^(a)	Water ^(b)	Oxygen	Water
1	LDPE	PA-6,6	737	7.05	35 (2)	160 (2)
2	LDPE	PA-6	654	6.78	31 (3)	154 (3)
3	HDPE	PA-6,6	195	3.70	31 (3)	273 (2)
4	HDPE	PA-6	176	3.58	28 (1)	256 (2)
5	LLDPE	PA-6,6	652	6.60	34 (1)	160 (2)
6	LLDPE	PA-6	647	6.57	34 (3)	163 (2)
7	HDPE	PA-6,6m	318	4.34	51 (4)	311 (4)

Notes: a) oxygen $P \times 10^{18}$ of 30 percent PA-blend ($\text{cm}^2/\text{Pa}\cdot\text{s}$) at 25°C, RH = 0 percent;
b) water $P \times 10^{11}$ of 30 percent PA-blend ($\text{g}/\text{cm}\cdot\text{s}$) at 37.8°C, RH = 90 percent.

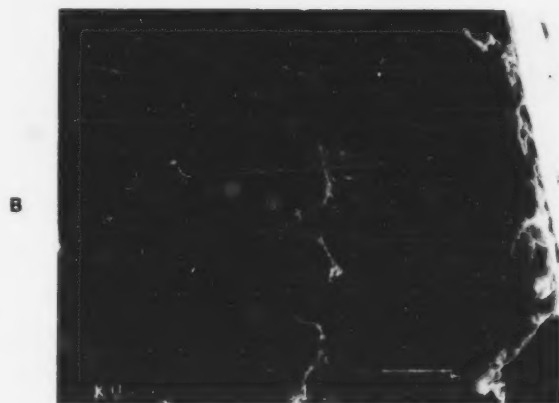


Fig. 5. SEM of HDPE with 20 weight percent of PA-6; A- untreated, B- acid-treated sample.

percent; Fig. 11) or an increasing concentration of cylinders (at 30 percent; Fig. 12). Detailed examination of the micrographs A reveals a physical separation of the phases; voids seem to exist around each PA intrusion in the PE matrix. The voids seem to be more pronounced for PA-6,6 than for PA-6 blends. It was expected that blends with PA-6,6m may show a better compatibility with PE. However, all the evidence indicates that this was not the case.

A



B

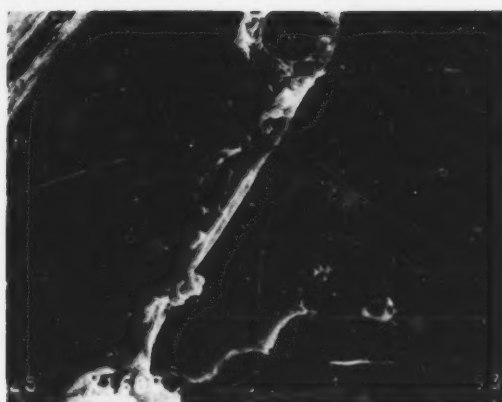


Fig. 6. SEM of HDPE with 20 weight percent of PA-6,6; A- untreated, B- acid-treated sample.

DISCUSSION

Oxygen Permeability

Both PE and PA are semicrystalline. Therefore, the permeability of gas through only one of these polymers involves two phases: amorphous and crystalline. Permeability through a blend of these two polymers would involve four phases, each of which has its own transport characteristics. However, assuming that the crystalline regions are impermeable, the two amorphous regions of polyethylene and polyamide should be considered.

Since the glass-transition temperature, T_g , of polyethylene is well below room temperature, it is most likely that the transport of oxygen through the polyethylene regions would be in accordance with the classical theory i.e., of pressure- and concentration-independent solubility and diffusion coefficients. However, since the T_g of dry polyamides is above room temperature, oxygen transport through their amorphous regions would follow the dual-sorption and partial-immobilization model (52). The situation becomes more complex when one considers factors such as phase separation, and

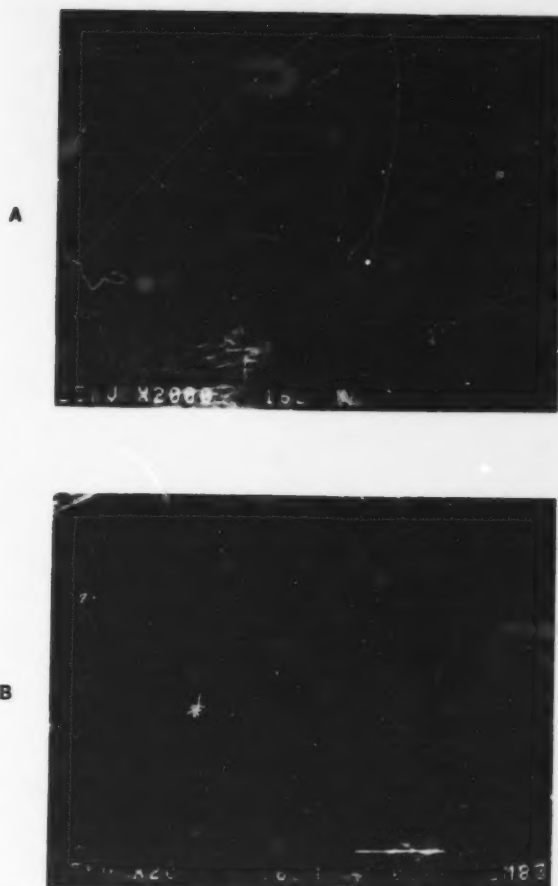


Fig. 7. SEM of HDPE with 20 weight percent of PA-6,6m; A- untreated, B- acid-treated sample

hence, discontinuity between phases, size distribution of the dispersed phase, variations in shapes of the dispersed phase, random orientation of dispersed domains, small contributions to the overall flux by crystalline regions, etc.

As expected, permeability measurements show that incorporation of polyamide reduces the oxygen permeability. Increasing PA content results in a larger reduction of oxygen permeability (viz. Figs. 1 and 2). Since the aim of this work was to reduce the oxygen permeability through commercial PE-based packaging films, it was deemed uneconomical to use more than 30 weight percent of PA. The effect of this loading on P and the ratio: P/P_1 are listed in Table 4. At this loading the oxygen permeability of the blends reduced to 28 to 35 percent of the original permeability of the polyethylene resin. The reduction was smallest in the case of the HDPE/PA-6,6m: 50.9 percent of the permeability of HDPE. These values are still at least one order of magnitude higher than the oxygen permeability of polyamide. The lowest oxygen permeability was obtained by combining HDPE and PA-6, while the highest values would be obtained by combining LDPE with PA-6,6m. The main reason for these variations is the crystallinity and relative thermal expansivity of the neat resins.

Evaluation of Permeability Models

An attempt was made to compare experimentally measured permeabilities with values obtainable from the previously discussed models. The blend films do not conform to the geometrical constraints employed in deriving the proposed relations. Furthermore, as shown by SEM, the shape of the dispersed phase changes with concentration of PA. However, the models may provide a guidance, upper-lower bounds, for future predictions of P . The four models were used: Maxwell; viz. Eq 4 with $f = 2$; Rayleigh; viz. Eq 4 with $f = 1$; series law, given by Eq 5; and parallel law, given by Eq 6.

An example of the calculation is presented in Fig. 13 for the LDPE/PA-6,6 blends. The dependencies for the other systems were similar. In all cases, the experimental curves were between the Maxwell and the series law predictions. The closest to the Maxwell equation was the system HDPE/PA 6,6m and then, in a sequence indicated, the others: HDPE/PA-6,6; HDPE/PA-6; LLDPE/PA-6,6; LLDPE/PA-6 = LDPE/PA6,6 = LDPE/PA-6.

The four models require that particle shapes and sizes be uniform, independent of concentration, and that the neat resin permeabilities remain unaffected by blending. As shown in Figs. 5 to 12 the

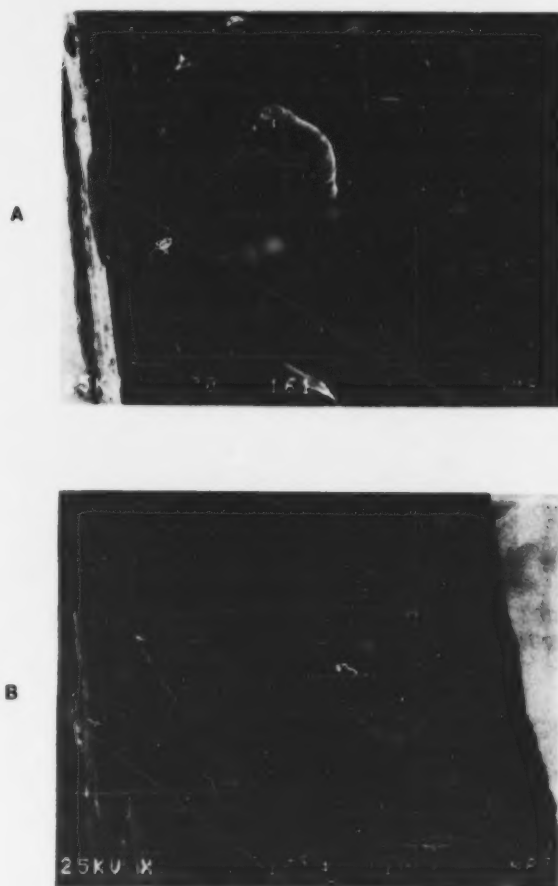


Fig. 8. SEM of LDPE with 20 weight percent of PA-6; A- untreated, B- acid-treated sample

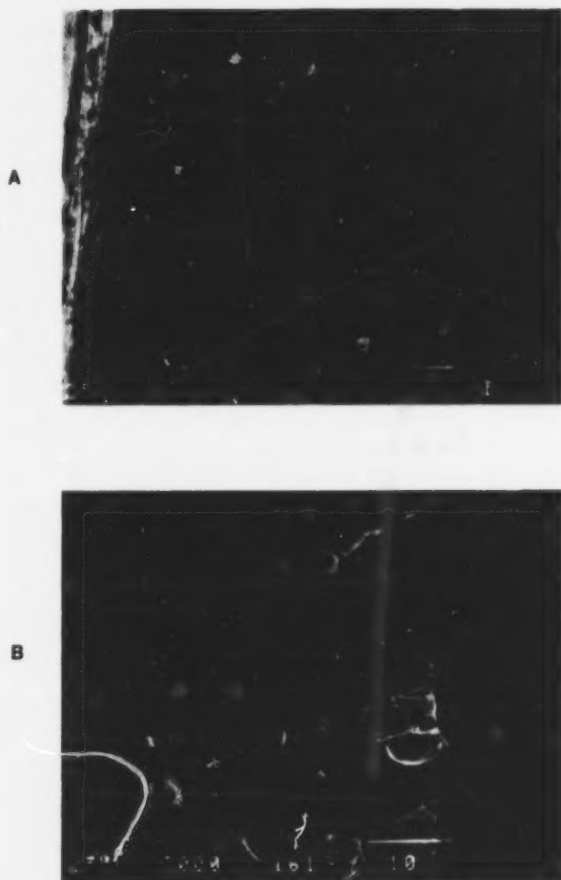


Fig. 9. SEM of LLDPE with 20 weight percent of PA-6; A- untreated, B- acid-treated sample.

geometrical assumptions are certainly not valid and, if the interphase separation indeed occurs, permeability of the interphase should also be taken into account. In view of the above, it is reasonable to expect the experimental curves of permeability at low concentrations to approach the Maxwell/Rayleigh curves with a tendency towards the Rayleigh curve at high concentrations. In general, this is in agreement with experimental observations, except that at the higher end of the concentration range, the permeability drifts rapidly downwards towards the series law. Although it is not evident from the photomicrographs, it is possible that, at higher polyamide concentrations, a PA-layering effect takes place.

Water Vapor Permeability Through Blends

Little work has been reported in connection with water vapor transport through polymers and, particularly, through polymer blends. Since gases seldom interact with polymers their permeability is relatively simple when compared to vapors. In particular, water vapor interacts with PA, resulting in sorption on hydrophilic sites, clustering, swelling of the polymer, etc. Since the temperature of measurement was higher than the glass-transition tem-

perature of the PE matrix, transport of water vapor should follow models of vapor transport in rubbery polymers, resulting in a diffusion coefficient increasing exponentially with concentration of the penetrant. However, it has been reported (53) that for PE/water the sorption and diffusion coefficients are independent of pressure and concentration, respectively, *i.e.*, due to very low H_2O solubility in PE the diffusion seemed to follow the classical theory. The PA's (at equilibrium in RH = 90 percent atmosphere) at $37.8^\circ C$ are plasticized by water and are also in a rubbery state, *i.e.* here the model transport of vapor through a rubbery polymer should be applicable.

In principle, the models used for O_2 permeability are not valid for H_2O -vapor. However, since there are no models which could relate water vapor permeability to the volume fractions of the components in a blend, it was decided to test their pragmatical usefulness. An example of the results is shown in Fig. 14, for LDPE/PA-6,6 blends. The data follow the Rayleigh equation quite well. Similar correlation was observed for the other systems containing LDPE or LLDPE; water permeability for the HDPE blends was found to be 40 to 60 percent higher than predicted by this equation. In Table 4, the H_2O -permeability for blends contain-

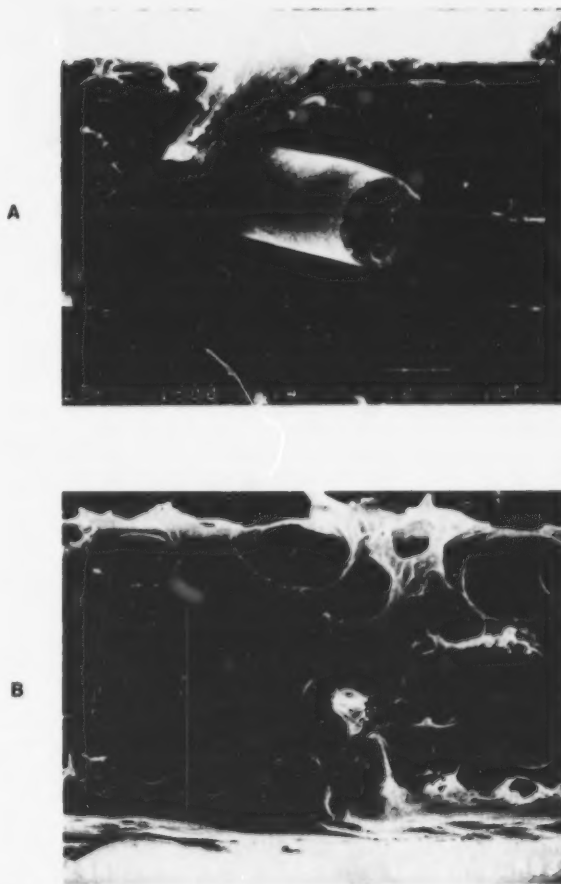


Fig. 10. SEM of LLDPE with 20 weight percent of PA-6,6; A- untreated, B- acid-treated sample.

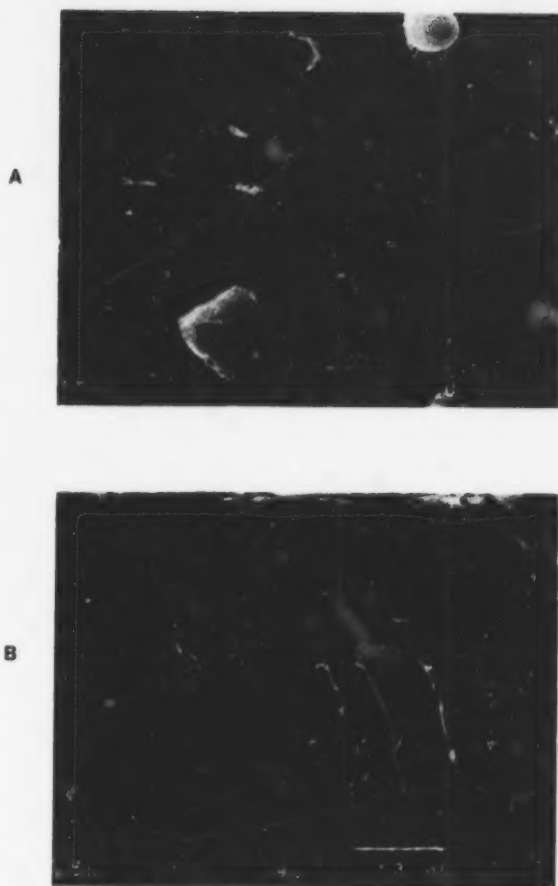


Fig. 11. SEM of LLDPE with 10 weight percent of PA-6,6; A-untreated, B- acid-treated sample.

ing 30 weight percent of PA as well as the relative permeability, $\bar{p}$, expressed in terms of percent of PE permeability are listed.

It should be noted that the water vapor permeability of HDPE is around 31 percent that of LDPE, while the permeability of LLDPE is around 93 percent that of the latter. Thus, P of LLDPE is somewhat between that of LDPE and HDPE, but much closer to the former. It is interesting to note that although water vapor permeability of PE is around 0.2 percent of the oxygen permeability, the relative permeabilities of the various types of polyethylenes to both oxygen and moisture still remain in the same order. This is probably due to the fact that the three types of polyethylene do not interact with either oxygen or water vapor and their crystallinity is the controlling factor.

The water vapor permeability of PA-6,6 is around 66 times larger than that of HDPE. On the other hand, P of PA-6,6 is within a few percent of the permeability of PA-6. Thus, in this case, the affinity of polyamides to water vapor is the dominant factor and it appears that the difference between the grades, effects of processing, and crystallinity are minimal. However, the water vapor permeability of the elastomer modified PA-6,6m is reduced to

about 44 percent that of the unmodified PA-6,6. This indicates that modification with the elastomer, which generally has less affinity to water vapor, contributes to a substantial reduction of polyamide permeability to water vapor. In any case, the water vapor permeability of HDPE/PA-6 blends is somewhat lower than that of HDPE/PA-6,6m blends. Therefore, the use of the PA-6,6m does not appear to be justified.

Incorporation of PA increases the H_2O permeability of PE; by about 60 percent for LDPE and LLDPE blends, but by 160 to 210 percent for HDPE blends. However, due to the low permeability of HDPE, the lowest water vapor permeability is obtained by combining HDPE with PA-6. The highest values are obtained by combining LDPE with PA-6,6. These observations are comparable to those obtained for oxygen permeability.

CONCLUSIONS AND RECOMMENDATIONS

The effect of PA addition on O_2 and H_2O permeability through PE film increases with PA-content. At the highest loading used in this study, 30 weight percent of PA, the most promising results were obtained for HDPE/PA-6; in this case permeability of O_2 decreased by a factor of 3.6 and that of H_2O

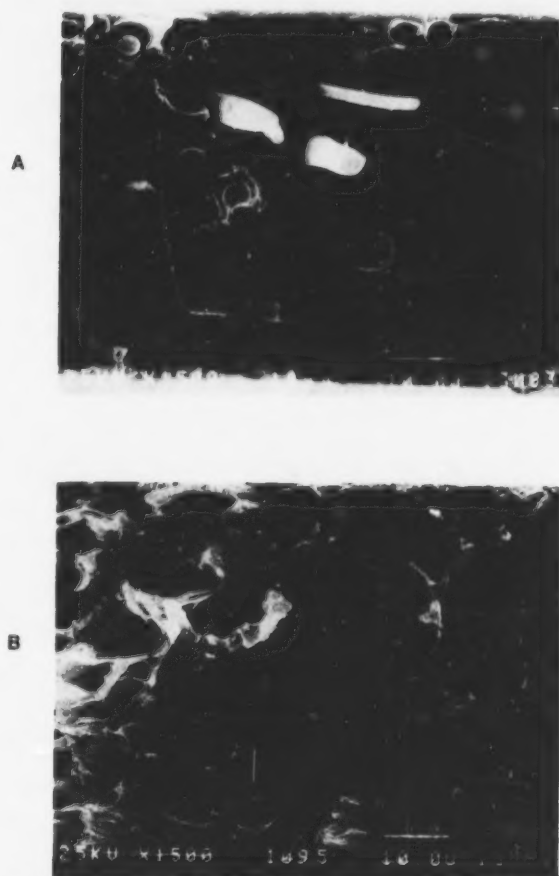


Fig. 12. SEM of LLDPE with 30 weight percent of PA-6,6; A-untreated, B- acid-treated sample.

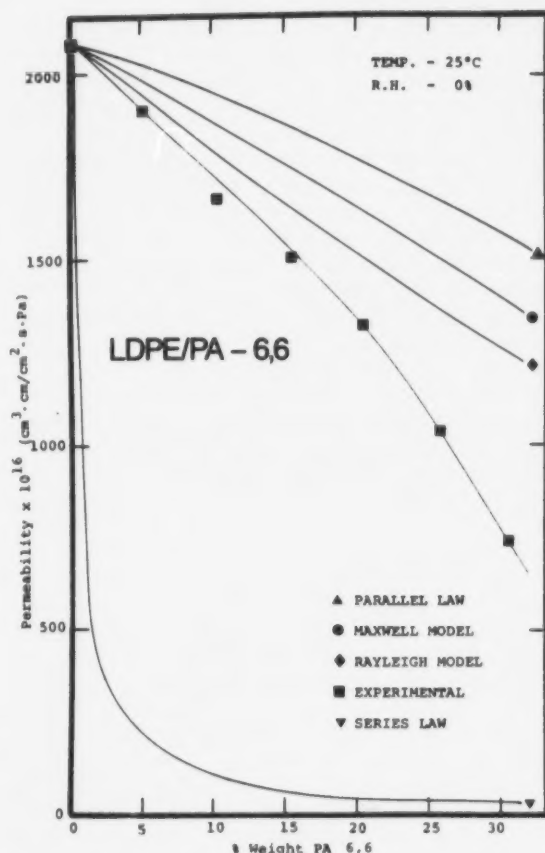


Fig. 13. Experimental and computed oxygen permeabilities for LDPE/PA-6,6 blends.

increased by a factor of 2.6. Overall, the least effective was incorporation of PA-6,6m; here the O_2 barrier properties were improved by 2.0 but H_2O worsened by 3.1.

At low polyamide concentrations, the experimental data were close to the Maxwell and Rayleigh models. Above 20 to 25 percent polyamide content, the experimental curves drifted towards the prediction of the series law, suggesting that at these high loadings a lamellar structure may be formed.

While the reported results are encouraging, a significant amount of work must be done before commercial utilization is possible; the thorough rheological studies of flow of these blends as well as evaluation of their mechanical properties should be carried out. Cost effectiveness of the blendings versus lamination or coextrusion should be examined as well. From the technical point of view the presented results indicate a need for more detailed study on the solubility and diffusion of gases and vapors through multicomponent systems: blends and composites. The effect of orientation of anisometric particles on permeability should also be undertaken.

ACKNOWLEDGMENTS

The authors wish to thank the following NRCC/IMRI personnel: Dr. K. Cole for the FTIR data on

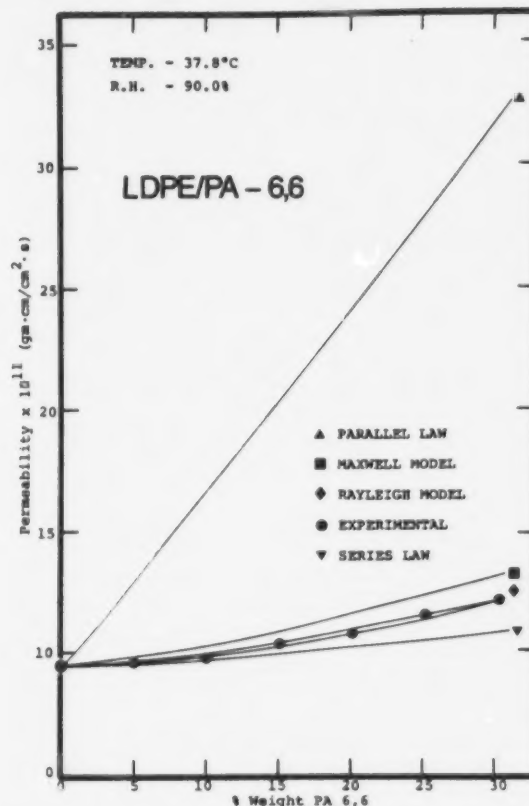


Fig. 14. Experimental and computed water vapor permeabilities for LDPE/PA-6,6 blends.

blend composition, Mr. M. Thibodeau for the SEM studies, Messrs. A. Catani, F. Hamel, P. Sammut, and Y. Simard for aiding in preparation of blends and measurements of permeabilities.

REFERENCES

1. H. J. Roder, *Kunststoffe*, **71**, 287 (1981).
2. K. A. Boni, U.S. Pat. No. 4, 102, 974 (1978).
3. U. Konig and H. L. Schuch, *Kunststoffe*, **67**, 27 (1977).
4. N. A. Peppas and R. Khanna, *Polym. Eng. Sci.*, **20**, 1147 (1980).
5. T. P. Labuza, L. McNally, D. Gallagher, J. Hawkes, and F. Hurtado, *J. Food Sci.*, **37**, 154 (1972).
6. T. P. Labuza, S. Cassil, and A. J. Sinskey, *J. Food Sci.*, **37**, 160 (1972).
7. H. E. Chou and T. P. Labuza, *J. Food Sci.*, **39**, 479 (1974).
8. R. J. Preto and Z. Scheckman, U.S. Pat. No. 3, 873, 667 (1975).
9. P. Forster and M. Herner, *Kunststoffe*, **69**, 146 (1979).
10. S. Lustig and J. Vicik, U.S. Pat. No. 4, 293, 664 (1981).
11. T. Graham, *Phil. Mag.*, **32**, 401 (1866).
12. S. von Wroblewski, *Wied. Ann. Physik.*, **8**, 29 (1879).
13. V. Stannett, *J. Membr. Sci.*, **3**, 97 (1978).
14. R. M. Felder and G. S. Huvar, "Methods of Experimental Physics," Vol. 16 C, R. Fava, ed., Academic Press, New York (1980).
15. J. Crank and G. S. Park, "Diffusion in Polymers," J. Crank and G. S. Park, eds., Ch.1, Academic Press, New York (1968).
16. C. A. Kumins and T. K. Kwei, "Diffusion in Polymer," J. Crank and G. S. Park, eds., Ch. 4, Academic Press, New York (1968).
17. V. Stannett, W. J. Koros, D. R. Paul, H. K. Lonsdale, and R. W. Baker, *Adv. Polym. Sci.*, **32**, 69 (1977).

19. J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 403 (1977).
20. J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 417 (1977).
21. C. E. Rogers, M. Fels, and N. N. Li, *Rec. Devel. Sep. Sci.*, **2**, 107 (1972).
22. V. Stannett, "Diffusion in Polymers," J. Crank and G. S. Park, eds., Ch. 2, Academic Press, New York (1968).
23. H. Fujita, "Diffusion in Polymers," J. Crank and G. S. Park, eds., Ch. 3, Academic Press, New York (1968).
24. A. Peterlin, *Controlled Drug Delivery*, **1**, 15 (1983).
25. A. Peterlin, *Makromol. Chem., Suppl.*, **3**, 215 (1979).
26. A. Peterlin, *J. Makromol. Sci., Phys.*, **B11**(1), 57 (1975).
27. A. S. Michaels and R. B. Parker, Jr., *J. Polym. Sci.*, **XLI**, 53 (1959).
28. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **L**, 393 (1961).
29. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **L**, 413 (1961).
30. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 413 (1963).
31. R. M. Barrer, J. A. Barrie, and M. G. Rogers, *J. Polym. Sci., Part A1*, 2565 (1963).
32. J. C. Maxwell, "Electricity and Magnetism," 3rd ed., Vol. 1, Dover, New York (1904).
33. W. I. Higuchi and T. Higuchi, *J. Am. Pharm. Assoc., Sci. Ed.*, **49**, 598 (1960); C. A. Peterson, *J. Appl. Polym. Sci.*, **12**, 2649 (1968).
34. W. J. Shrenk and T. Alfrey, *Polym. Eng. Sci.*, **9**, 393 (1969); T. M. Connelly and J. C. R. Turner, *Chem. Eng. Sci.*, **34**, 319, (1979).
35. J. Sax and J. M. Ottino, *Polym. Eng. Sci.*, **23**, 165 (1983).
36. J. M. Ottino and N. Shah, Paper presented at "Polyblends-83," Montreal, (1983); *Polym. Eng. Sci.*, **24**, 153 (1984).
37. B. G. Ranby, *J. Polym. Sci., Part C*, **51**, 89 (1975).
38. Y. J. Shur and B. G. Ranby, *J. Appl. Polym. Sci.*, **19**, 1337, 2143 (1975); *ibid.* **20**, 3105, 3131 (1976).
39. L. M. Robeson, A. Noshay, M. Matzner, and C. N. Merriam, *Die Angew. Makromol. Chem.* **29/30**, 47 (1973).
40. P. Masi, D. R. Paul, and J. W. Barlow, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 15 (1982).
41. H. Odani, K. Taira, N. Nemoto, and M. Kurata, *Polym. Eng. Sci.*, **17**, 527 (1977).
42. J. A. Barrie and K. Munday, *J. Membr. Sci.*, **13**, 175 (1983); J. A. Barrie and J. B. Ismail, *ibid.*, **13**, 197 (1983).
43. M. Matzner, D. L. Schober, R. N. Johnson, L. M. Robeson, and J. E. McGrath, *Org. Coat. Plast. Prepr.*, **34**, 469 (1974).
44. Anonym, "Modern Plastics Encyclopedia," McGraw Hill (1981-82).
45. Anonym, "Design Handbook," Du Pont Zytel Nylon Resins (No. E-06167).
46. H. B. Hopfenberg and D. R. Paul, "Polymer Blends," D. R. Paul and S. Newman, eds., Ch. 10, Academic Press, New York (1978).
47. G. Illing and J. Arndt, *Kunststoffe*, **72**, 87 (1982).
48. S. Anavi, M. T. Shaw, and J. F. Johnson, *Macromolecules*, **12**, 1227 (1979).
49. L. A. Utracki and G. L. Bata: Polymer alloys: CANPLAST '81, Montreal, Quebec, Oct. 25, 1981, proceedings.
50. L. A. Utracki and G. L. Bata: Alliages Polymériques: Quoi, Quand, Comment et Pourquoi? Part I and II, *Matériaux et Techniques (Paris)*, **70**, 223 (1982), *ibid.* **70**, 282 (1982).
51. L. A. Utracki, RETEC Montreal, 1982; Proceedings: *Polymer Plastics Technol. Eng.*, **22**, (1), 27 (1984).
52. J. H. Petropoulos, *J. Polym. Sci., Part A-2*, **8**, 1797 (1970).
53. H. Yasuda and V. Stannett, *J. Polym. Sci.*, **57**, 907 (1962).

DISCUSSION

W. E. Baker: Your comment about applicability of this technology to film puzzles me. Perhaps you are aiming this at the thin-wall container market. A much more economical way of arriving at these properties is coextrusion, lamination, or use of a small amount of EVA. Can you explain the background and application of this project.

L. A. Utracki: First of all, I do not subscribe to your

theory that blending is less economical than coextrusion. To coextrude you need more capital investment. Furthermore, the process is more sophisticated and more expensive. The additional cost for coextrusion, is probably from \$0.5 to 0.7 per pound. Blending, as done in this work, requires the same extrusion line as that for a standard PE. To be certain, one has to dry PA and use it at somewhat higher concentration than in coextrusion. The method can accommodate EVA. Furthermore, incorporation of PA is expected to improve the mechanical properties of PE thus allowing reduction of the film thickness. As to the background of this project, it was initiated by two processors—one a film manufacturer, the other a milk carton producer. The aim was to provide a simple, economic method of oxygen permeability reduction by about 30 percent for extruded films and laminated cardboard containers without modification of the existing process equipment. So far we have demonstrated viability of the blending method—nothing more and nothing less. The process has not been optimized and evaluated on the production line. On the other hand we obtained up to 360 percent reduction of oxygen permeability with relatively small increase in water permeability. The method can be applied to thin-wall injection or blowmolding. The "Selar" from Dupont, recently available on the market, can be used in a similar way.

J. M. Charrier: Dr. Baker alluded to mechanical properties. I agree that on the purely economic basis your material may be competitive, but what about the mechanical properties—tensile strength, dart impact . . .

L. A. Utracki: We expect that the mechanical properties of PE/PA film have improved. We see the crystalline PA-dispersed phase as elongated fibrillar-like, reinforcing intrusions into the PE-matrix. The effect must be sensitive to the degree of orientation generated during the process and to the earlier extrusion conditioning. So far we have not measured the melt-flow properties. Nor have we extruded on an industrial line or not examined the mechanical behavior. We observed large differences in mechanical properties due to orientation/deformation of the dispersed phase in other incompatible polymer blends.

C. Sadr: We all know that PA and PE are incompatible. Even after only 5 percent PA the impact or elongation properties are very bad. First of all I do not know how you can get good barrier by mixing PA with PE. The second question: if the process becomes commercial how will people reprocess these materials? If you recycle the blend you destroy the layers and will simply be left with a scrap.

L. A. Utracki: It seems that I have already answered your comment regarding the mechanical properties. We are quite aware that these two resins are incompatible and if orientation caused by film or bottle blowing will not do the trick, we shall have to compatibilize. We have ideas how to do this, but it may not be necessary. For cardboard lamination the mechanical properties are not important—they are provided by the cardboard itself. The reason

for getting good barrier properties is simply the low oxygen permeability of the dispersed PA phase. As the analysis of permeability indicates, the barrier properties strongly depend on morphology—the most efficient is a series of lamellas, the least efficient a spherical dispersion. Our case is in between these two—close to spheres at low loading, and close to lamellas at high loading. Regarding the recycling: your argument in effect provides support for the proposed blending method; it is true that coextruded films cannot be recycled to generate films which behave similarly, but blends can be reprocessed, regenerating essentially the same properties. The reprocessability of blends is a big selling point for the DuPont Sclar technology.

A. Rudin: The barrier properties will depend on detailed morphology as you pointed out. Is it possible to control the morphology in such processes as blowmolding or blown-film extrusion so as to generate sheets of the barrier material interspersed in the matrix. Is this possible without a fancy die?

L. A. Utracki: Yes. This is a relatively straightforward process. There are three conditions: lower viscosity of PA than that of PE at the extrusion temperature, a proper concentration of PA, and the divergent flow. When these conditions are met the

laminar structures are to be expected. The thermodynamics can help create this morphology, but this is not essential. Such a method of morphology control is already used in industry.

G. Vexler: Did you contemplate using higher nylons like "6,9", "6,10" or "12". In spite of increased cost you may have a synergistic effect due to longer hydrocarbon sequences.

L. A. Utracki: We considered PA-11. However, there are two arguments against this route: the cost and the reduced barrier properties of the higher nylons. You may be right about the synergism, but in the time allotted we decided to try the other, more common nylons. If the compatibility is a problem then maybe we shall try a mixture of PA-6 with PA-11 or PA-12.

H. P. Schreiber: This was a very nice paper, Leszek. The permeabilities you reported—are these single values for these materials or do they depend on the thermal history or process conditions?

L. A. Utracki: They are *not* single values. the permeability strongly depends on morphology, which on the other hand is affected by the processing. To estimate the magnitude of the effect one can use the two limiting equations—the parallel and series laws. The experimental data are between these two.

Preliminary Results on Toughening a Linear-Low-Density Polyethylene Using Thermoplastic Elastomers

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The effects of several commercially available thermoplastic elastomers (TPE) on a gas-phase linear-low-density polyethylene (LLDPE) were studied using small-scale commercial-compounding techniques. The properties of blown films of these compositions were evaluated as a function of TPE type and composition and compared to unmodified LLDPE films. Ethylene/propylene elastomers had modest effects on the falling-dart impact strength and machine-direction tear propagation resistance while polyisobutylene and styrene block copolymers had more significant effects on these properties.

INTRODUCTION

Over the last ten years relatively few new polymer materials have evolved, primarily because of the major costs involved. Filling the gap has been a growing interest in the less costly development of polymer blends in which the attractive properties of two or more different polymers are combined to yield commercially viable materials, some with thermodynamic properties of a completely new material. Some studies have concentrated on the theory of blends (1), the rheology of blends (2 to 4, 23), and the methods of preparation (5 to 7). More specifically, several investigations have concentrated on the toughening of various plastics with thermoplastic elastomers (8 to 15).

A relatively new family of polymers destined for wide use, particularly in film, is the gas-phase linear-low-density polyethylenes (LLDPE). The first generation of butene copolymers made by this process have low machine-direction (M. D.) tear resistance characteristics and only average dart-drop impact strength when processed into film. However they exhibit many good physical properties otherwise and are produced at relatively low cost. Because of their newness, little published data regarding blends of these materials exists. Methods of upgrading the film toughness (impact strength, tear resistance) of these materials by blending with different thermoplastic elastomers are explored in this paper.

EXPERIMENTAL

Materials

The experimental program consisted of preparing blends of a particular grade of gas-phase linear-low-density polyethylene with one of several thermoplastic elastomers. The polyethylene had a melt index of 1.0, a density of 0.919, and a narrow molecular weight distribution. The elastomers, described in Table 1, include two ethylene/propylene elastomers (E/P I and E/P II), a polyisobutylene (B I), a polyisobutylene/isoprene copolymer (B II), two styrene/ethylenebutylene/styrene copolymers (SEBS I and SEBS II), a styrene/isoprene/styrene copolymer (SIS), and a styrene/butadiene/styrene copolymer (SBS).

Blending

The blends were prepared in one of two ways, either by dry blending the elastomer in pellet, nib, or crumb form with the granular LLDPE or by preparing a high-concentration compound of the elastomer (in a BR Banbury model) which was subsequently blended with the LLDPE. The Banbury compounds were all produced under the same conditions arrived at during preliminary trials. A one-kilogram total charge was loaded in the following sequence: the LLDPE plus antioxidant, followed by the elastomer either cut in chunks from bales or in granular form. The compound usually consisted of

Table 1. Properties of Elastomers*.

	E/P I	E/P II	B I	B II	SIS	SEBS I	SEBS II	SBS
Chemical Type	Ethylene propylene	Ethylene propylene	Isobutylene homopolymer	Isobutylene isoprene	Styrene/isoprene (block)	Styrene/ethylenebutylene (block)	Styrene/ethylenebutylene (block)	Styrene/butadiene (block)
Composition	75% ethylene 25% propylene Pellet	50% ethylene 50% propylene Bale	Bale	0.7% isoprene 99.3% isobutylene Bale	86% isoprene 14% styrene Crumb	72% ethylenebutylene 28% styrene Fine granule	71% ethylenebutylene 29% styrene Fine granule	57% butadiene 43% styrene Pellet
Available								
Density (kg·m ⁻³)	0.860	0.860	0.920	0.920	0.920	0.920	0.920	0.960
Melt index (g/10 min)	0.74	0.3	0.6	0.03	13.3	0.04	0.7	9.8

* Properties of Elastomers were provided by Loco Inc., Shell Chemical Co., Exxon Chemical Co., and Polysar Inc.
* ASTM D-1558 (round-E).

50 percent elastomer. The kneading consisted of one minute at 225 rpm, followed by a pressure release to atmosphere and then 4 minutes at 100 rpm keeping the temperature at 150°C $\pm$ 3°C. The batches were dumped after the cycle, cut into pieces, and later granulated.

Film Extrusion

The dry blends of the LLDPE and elastomers or elastomer compounds were added to the stirred hopper of a 65 mm, 4-zone film extruder modified for LLDPE. The film was blown through a 150 mm medium-pressure spiral die with a melt temperature of 230 to 245°C and an output of about 0.9 kg. per hour per centimeter of die circumference. The film thickness was 37 microns and the width was 52 cm corresponding to a blow-up ratio of 2 to 1.

Testing of Films

The mechanical properties were evaluated as follows:

Tensile Strength
Yield Strength
Elongation
Stiffness—ASTM D-882
Tear Propagation Resistance—ASTM D-1992
Dart Drop Impact Strength—ASTM D-1709

RESULTS AND DISCUSSIONS

The gas-phase LLDPE resins offer the blown film manufacturer and the end-user the advantages of good drawdown, attractive price, and availability. Films made from these resins display higher tensile strengths at yield and break, higher elongations, and higher puncture energies than high-pressure LDPE. However they have the drawback of generally low machine-direction tear propagation resistance and fairly low dart-drop impact strength particularly when compared against the higher alpha-olefin solution type LLDPEs. In this preliminary study no attempt was made to optimize the selection of the elastomers within each family studied. The first material in each of the *Tables 2 to 4* is the control film made without elastomer. They are representative of commercial films having typical tear, impact, and tensile properties. The major variables looked at were the percentage of elastomer in the film, the type of elastomer, and whether the elastomer was dry-blended or precompounded.

E/P I, II Elastomers

In *Table 2* the first 3 films modified with E/P I crumb show declining tensile properties and stiffness as expected. Both the impact and tear resistance increase although the increases appear insignificant below 15 percent elastomer addition. When the 15 percent E/P I was incorporated in a Banbury compound form there was not much dif-

Table 2. Effect of Addition of E/P Elastomers on LLDPE Film Properties.

No.	Rubber type	None	E/P I	E/P I	E/P I	E/P I	E/P I/E/P II	E/P II
	% Rubber in Film	0	10	15	20	15	6 E/P I 9 E/P II	15
	Form of rubber blended with LLDPE on film line	—	Pure crumb	Pure crumb	Pure crumb	Banbury compound	Banbury compound	Banbury compound
1.	Tensile M.D.* at break T.D.** (MPa)	26.9 24.7	22.3 24.0	26.4 25.1	23.8 21.8	28.6 24.3	26.6 24.3	26.2 24.1
2.	Tensile M.D. At yield T.D. (MPa)	8.5 9.6	8.0 8.6	8.9 9.1	7.6 7.7	8.4 9.1	8.5 8.9	8.1 8.6
3.	Elongation M.D. At break T.D. (%)	638 644	519 588	560 570	556 581	525 550	590 660	580 675
4.	Stiffness M.D. (MPa) T.D.	212 241	176 206	151 162	158 183	152 170	136 155	128 144
5.	Tear propagation M.D. Resistance T.D. (g/25 μ m)	157 293	164 325	229 342	196 346	214 357	159 296	177 303
6.	% Change in M.D. Tear Dart impact (g/25 μ m)	— 75	+4 85	+46 99	+25 97	+36 106	+2 110	+13 126
	% Change in impact	—	+13	+32	+29	+41	+47	+68

Notes: * M.D.—Machine direction.
 ** T.D.—Transverse direction.

Table 3. Effect of Addition of Isobutylene Elastomers on LLDPE Film Properties.

No.	Rubber type	None	BI	BI	BI
	Percent rubber in film	0	15	15	15
	Form of rubber blended with LLDPE on film line	—	Banbury compound	Banbury compound	Banbury compound
1.	Tensile M.D. at break (MPa) T.D.	27.9 25.8	21.4 21.3	23.3 20.6	23.2 23.6
2.	Tensile M.D. at yield (MPa) T.D.	10.4 11.8	8.6 9.2	8.3 9.2	8.2 8.6
3.	Elongation M.D. at break (%) T.D.	550 600	530 560	540 550	600 660
4.	Stiffness (MPa) M.D. T.D.	196 227	155 172	164 181	139 157
5.	Tear propagation M.D. resistance (g/25 μ m) T.D.	156 283	247 331	260 295	217 319
6.	% Change in M.D. tear Dart impact (g/25 μ m)	— 72	+58 120	+67 114	+39 142
	% Change	—	+67	+58	+97

Table 4. Effects of Addition of Styrene Copolymer Elastomers on LLDPE Film Properties.

No.	Rubber type	None	SBS	SBS	SBS	SIS	SIS	SEBS I	SEBS II	SEBS II
	% Rubber in film	0	10	15	20	10	20	15	10	20
	Form of rubber blended with LLDPE on film line	—	Pure Pellets	Pure Pellets	Pure Pellets	Pure crumb	Pure crumb	Pure granule	Pure granule	Pure granule
1.	Tensile at break (MPa) M.D. T.D.	23.8 22.9	24.2 20.7	25.3 20.7	23.4 23.3	20.2 18.0	17.8 14.9	23.5 25.6	24.6 21.4	22.9 24.7
2.	Tensile at yield (MPa) M.D. T.D.	9.9 10.9	8.5 9.0	7.9 7.9	7.8 7.4	8.4 8.2	7.1 6.7	8.3 8.9	8.5 8.7	6.8 7.3
3.	Elongation at break (%) M.D. T.D.	550 580	606 581	560 540	606 663	560 540	575 525	460 520	525 525	420 520
4.	Stiffness (MPa) M.D. T.D.	217 242	190 195	177 146	185 157	198 196	147 148	138 151	158 189	148 148
5.	Tear propagation Resistance (g/25 μ m) M.D. T.D.	141 298	176 270	197 261	208 277	201 310	306 298	161 232	187 317	141 245
6.	% Change in M.D. tear Dart impact (g/25 μ m)	— 60	+25 124	+40 162	+48 177	+43 86	+117 148	+14 >222	+33 111	0 >235
	% Change in impact	—	+107	+170	+195	+43	+147	>270	+85	>292

ference in property improvement to what was achieved with the direct use of crumbs. The last two films in Table 2 show the progressive replacement of the E/P I with E/P II at a constant elastomer

content of 15 percent. In this case the tear properties drop but the impact properties improve noticeably and the stiffness drops even further.

In the case of the E/P rubbers it is not clear

whether the elastomer actually forms a discrete discontinuous phase or is located in the amorphous regions of the LLDPE influencing the polyethylene spherulite formation. These films were fairly clear but this observation could suggest either the later structure or one in which the dispersed-phase particles are so small that they are not seen with visible light (17). The fact that the higher molecular weight E/P II gave greater impact improvement could indicate either its effect on reducing the polyethylene spherulite size (19) or changing the elastomer domain size toward a preferred critical size (20, 21).

Isobutylene Elastomers

The next class of elastomer evaluated was based on isobutylene. These are tacky polymers, available in bales only, and hence they must be compounded in order to get them in a form such that they could be blended with LLDPE granules. Referring to Table 3, one can see the effect of addition of 15 percent of each of the two polyisobutylene type elastomers to LLDPE. Again the addition of elastomer leads to reduced stiffness and tensile strengths at yield and break. The tear strength is much higher particularly for B I and the impact strength is much higher particularly for B II. A limited number of examinations of these films were made on a phase-contrast microscope. All three films made in this group showed considerable heterogeneity and were very hazy compared to those made with the E/P elastomers suggesting that these polyblends consist of a discrete dispersed elastomer phase in the LLDPE. It is not clear whether the haziness is primarily caused by elastomer particle-induced surface roughness (16), the difference in refractive indices of the blend components (17), or the size and orientation of the elastomer domains (18). It does indicate, however, that some degree of incompatibility, yielding a domain structure, is helpful in improving impact strength in this system (18). This, in turn, suggests that the conditions for preparing these types of compounds and films may have a very significant effect on final properties (20 to 22).

A brief comment can be made at this point about the reproducibility of both the film-making procedure and the compounding procedure. A comparison of the properties of the control films in Tables 2 and 3 show good reproducibility of all properties with the possible exception of tensile strength at yield. In Table 3 two films are described each made with 15 percent compounded B I elastomer. Their properties are very similar indicating the general reproducibility of the techniques used.

Styrene Copolymer Elastomers

The last class of elastomers evaluated were the block copolymers of styrene; SBS, SIS, and SEBS. These materials are usually available in crumb or granule form. Table 4 shows results for tests made only by dry blending the elastomer pellets, crumbs, or granules with the LLDPE. Generally these styrene copolymer blends have lower tensile and stiffness properties as do the first two families of elas-

tomers but tend to have higher tear and impact strengths depending on the type of styrene copolymer involved. The SIS elastomer yields noticeably lower tensile improvement but the best tear strength improvement. The SIS and the SEBS give the greatest stiffness reduction. The increased impact strengths achieved with these elastomers are significant. The greatest improvements in impact are imparted by the higher molecular weight SEBS I followed by the lower molecular weight SEBS II and then the SBS type. The addition of only 10 percent SBS results in over 100 percent impact improvement while the addition of 15 percent SEBS II results in over 270 percent impact improvement.

The microscopic examination of the films in this family does not result in large differences in transparency with the exception of SEBS I. The SBS modified film had moderate transparency, while the SEBS II was quite transparent. The SEBS I had large heterogeneities in it. The poor dispersion in the latter case is likely a result of the viscosity mismatch between the LLDPE and the SEBS I leading to some very large and ineffective elastomer domains. Nevertheless the impact improvement is large. In contrast, the clear SEBS II shows good impact improvement too. In these blends involving styrene based elastomers, the elastomer likely forms a discrete phase. The effects of the center block composition, molecular weight, and method of blend preparation on morphology and hence film properties are complex and require considerably more study.

Figures 1 and 2 summarize the tear and impact improvements found in Tables 2 to 4 in a bar-chart format. The results on tear improvement show that the isobutylene polymers and the SIS polymers offer the best relative improvement with the maximum being in the order of 60 to 100 percent. Figure 2 shows that the best impact improvements are realized by the SEBS type styrene copolymers with maximum improvements in excess of 270 percent. As mentioned earlier the E/P elastomers used in this study rank inferior to the isobutylene and styrene elastomers. Even if attempts were made to

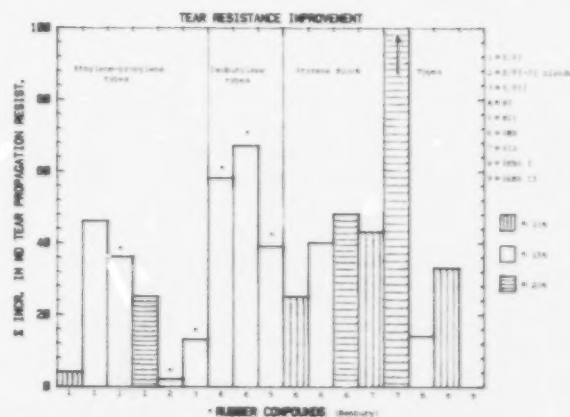


Fig. 1. Summary of the effect of elastomers on tear propagation resistance.

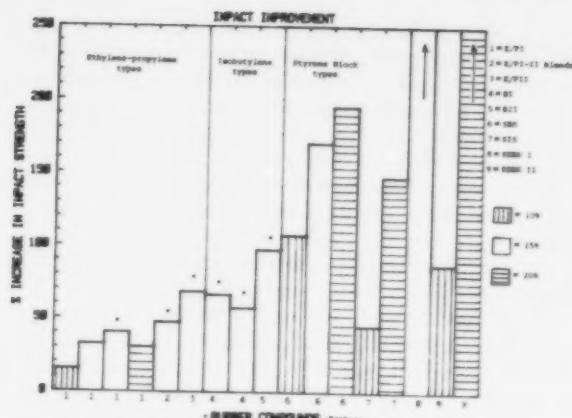


Fig. 2. Summary of the effect of elastomers on impact strength.

optimize the E/P elastomer or EPDM it is unlikely that the same improvements would be achieved as those with optimized selection of the other two elastomer types.

CONCLUSIONS

1. With the limited number of elastomers studied it has been found that the styrene-based elastomers give the greatest toughness improvement, followed by the polyisobutylene and then the ethylene/propylene elastomer.
2. The improvements in the LLDPE toughness were not related to chemical structure similarities between the LLDPE and the elastomer family tested. Rather, the seemingly incompatible elastomers performed better.
3. The methods and the degree of dispersion used to prepare the LLDPE/EPR systems did not have a major influence on toughness.
4. The LLDPE/PIB systems which showed considerable toughness improvement should be evaluated using different compounding conditions.
5. The LLDPE/SEBS and the LLDPE/SBS systems, which were made without any precompounding should be evaluated using different compounding techniques.
6. A close examination of the relationship between morphology and film properties should be made particularly with the PIB and the styrene copolymer blend systems.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contribution of Leco Inc. in producing and testing the films and of ESSO Chemical Canada Ltd. for providing the polyethylene resin used in the study.

REFERENCES

1. R. Prud'homme, *Polym. Eng. Sci.*, **22**, 90, (1982).
2. H. P. Schreiber, *Polym. Eng. Sci.*, **19**, 900, (1979).
3. A. P. Plochocki, *Polym. Eng. Sci.*, **23**, 618, (1983).
4. L. A. Utracki and M. R. Kamal, *Polym. Eng. Sci.*, **22**, 96, (1982).
5. Anonym, *Plastics Compounding*, **20**, No. 1, (1981).
6. M. T. Shaw, *Polym. Eng. Sci.*, **22**, 115, (1982).
7. H. Kapuscinski and H. P. Schreiber, "Effects of Thermo-Mechanical History on Polymer Blend Properties," presented at the SPE Antec Montreal, April, 1977.

8. A. Garshman, *Plast. Technol.*, **59**, No. 6, (1978).
9. G. Loyer, *Caoutchoucs et Plastiques*, **71**, No. 624, (1982).
10. G. Holden, "Current Applications of Styrene Block Copolymers," Paper presented at "Canplast '82", SPI, Toronto, Sept., 1982.
11. H. P. Schreiber, "Polyolefin/Elastomer Blends, The Effect of Thermal and Shear History," presented at the SPE Antec, May, 1981.
12. C. S. Wang, *Polym. Eng. Sci.*, **23**, 530, (1983).
13. P. A. DePaulo and D. P. Da Via, *Plastics Compounding*, **90**, No. 6, (1979).
14. Anonym, *Engineering*, **1**, March 1983.
15. J. M. Wefer, *J. Elastomers Plastics*, **15**, 43, (1983).
16. T. F. Reed, H. E. Bair, and R. G. Vadimsky, "Recent Advances in Polymer Blends, Grafts and Blocks," Plenum Press, New York (1974).
17. R. S. Stein, "Optical Behavior of Polymer Blends," D. R. Paul and S. Newman, eds., Academic Press, New York (1978).
18. R. J. Tabar, S. R. Hu, and R. S. Stein, *J. Appl. Polym. Sci.*, **28**, 1409 (1983).
19. M. Kryszewski, A. Faleski, T. Pakula, J. Grebowicz, and P. Milczarek, *J. Appl. Polym. Sci.*, **15**, 1139 (1971).
20. W. M. Speri and G. R. Patrick, *Polym. Eng. Sci.*, **15**, 668 (1975).
21. J. M. Starita, *Trans. Soc. Rheol.*, **16**, 339 (1972).
22. Z. K. Walczak, *J. Appl. Polym. Sci.*, **17**, 169 (1973).
23. Gh. Adamescu, M. Rusu, S. Petrovan, M. Lungu, and N. Asandei, *Acta Polymerica*, **32**, Heft 11, 704 (1981).

DISCUSSION

A. A. Alim: Could you comment on the difference in processability of these different blends.

W. E. Baker: We actually saw very little difference on the film line. The only thing which we noticed was the variation of the back pressure. We did not observe any difference on the amps. Over the whole family of blends the back pressure, and the output, did not vary by more than 15 percent to my surprise.

A. A. Alim: This is surprising! I noticed that your die rate was relatively low: 0.9 kg/cm. I wonder if at higher rates you would observe the same trend or not.

W. E. Baker: Well, I think that you would get poorer control at the higher outputs. These results are actually good for straight LLDPE. In the second phase of this study we did increase the rates, lowered the blow-up ratio, increased the output, and dropped the gauge. All these three elements gave us a weaker film and as a result we had to go to the second condition of dart-drop test with the 60-inch drop in order to have film breakage. In short, under these second processing conditions we started to spread the numbers much further apart. However the trend on impact, if anything, was improved.

C. Sadr: What about die swell? Any difference with EP and SBS?

W. E. Baker: We did not see any melt fracture in the film making. As far as die swell—we neither observed it nor especially looked for it. With LLDPE we did worry about melt fracture. This would complicate the method of evaluation of properties.

Y. Ilahie: What was the antioxidant system you used?

A. M. Catani: Irganox 1076 with 1024 at 0.1 percent of each.

Y. Ilahie: When you are putting in these rubbers,

there is a significant drop in stiffness. I wonder if LLDPE with lower density (to match the stiffness of these rubber modified blends), would be equal in impact performance.

W. E. Baker: I would love to see a sample of LLDPE with density well below 0.919 (g/ml). However, I doubt that you would get the stiffness sufficiently low to get 250- to 300 percent impact improvement. But your question regarding the evolution of resins coming out of the Unipol process is important. It should be recognized that the process is in an early stage of evolution and new interesting grades appear every quarter.

Y. Ilahie: You mentioned that the 1-butene copolymers are inferior to solution-produced octene monomer-type materials such as Dowlex or Sclair II. I would like to mention that the gas-phase technology can and is being used to produce materials with high-molecular-weight alpha-olefin comonomers up to 1-octene. These are equal in performance to the solution resins.

W. E. Baker: I have seen some of the hexene copolymers but not any of the octene gas-phase types yet. I will go on the line and say that the 300 percent impact improvement is not going to be easy to achieve by this route. The improvements we presented today are significant, going beyond what can be obtained even from the solution octenes.

A. A. Alim: We have seen about 100 percent improvement on the tear and about 200 percent on impact.

W. E. Baker: This is very good. I look forward to seeing some of these materials soon.

Y. Ilahie: Can you comment on the economics of this technology.

W. E. Baker: Only in a limited manner. The econom-

ics may not be too good against these higher alpha-olefin copolymers. Blending stands very well against the butene varieties, but I have to recalculate the economics against the newer materials. The PIB is the least expensive rubber but as you saw, it was not the highest performer. The SEBS block polymers are the most expensive and these are the best. So one has to carefully assess the economic parameters.

L. A. Utracki: I have a comment regarding copolymerization versus blending. From the rheological point of view the results are usually quite different, leading to different sets of properties, especially for blends of linear polymers with complex materials—rubbers or block polymers of the SEBS type. Rubbers and blocks may generate yield stress, which can be translated as equivalent to very high molecular weight. At the same time the high shear viscosity may be hardly different, i.e. the M.I. will be close to that of the neat resin. In other words, blending with rubbers or blocks generates not only very broad molecular weight distribution but also a multimodal one, difficult to reproduce in a single-stage polymerization process. Blending efficiently translates LLDPE into material similar in behavior to the high-pressure PE. I feel that lowering the density will result in linear molecules with a higher degree of short branches—a system which will not be able to reproduce the degree of entanglement density obtained by Baker and Catani. A question: did you evaluate the creep behavior of your films?

W. E. Baker: No. This is a cosponsored project with a commodity film extruder and their interests are in the impact, tear, and tensile behavior. It will be worthwhile to look, among other things, at creep as well.

Ultrasonic velocity measurement for the determination of density in polyethylene

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An ultrasonic immersion method is presented for the rapid and accurate measurement of longitudinal sound velocity (v) in polyethylene (PE). The method is based solely on the measurement of time delays and can be automated. The samples are the same press-molded plaques that are prepared for the standard-density (ρ) determination using a density-gradient column. Our measurements on a representative group of various types of PE with densities in the range 0.92 to 0.96 g/cm³ show without ambiguity that v is proportional to ρ . The degree of correlation is such that we come to suggest that the acoustic method be used for the characterization of density. We show that the accuracy is good and compares with that of the density-gradient column and we then conclude on the practical advantages of the ultrasonic method.

INTRODUCTION

Polyethylene possesses a number of physical properties that make it a very interesting basic industrial material. These properties depend in part on the mode of processing and they can be more or less adjusted to product requirements. This feature, which makes for a material having a wide range of applications, together with the fact that polyethylene is relatively inexpensive explains why it has become one of the most important commercial thermoplastics. Many possible grades of polyethylene (PE) exist, corresponding to different polymerization mechanisms, and it is of primary importance for the producer and the processor to have available methods for characterizing the polymer.

In a somewhat simplistic manner, PE can be viewed as a binary mixture of an amorphous and a crystalline phase. The degree of crystallinity affects properties such as the elastic moduli, the impact strength, the melting point, and others. However, it is known (1) that density (ρ) is directly related to the degree of crystallinity. Thus in the relationship between the basic parameters of PE and its end properties, the density value is an important link. This explains why density has always been the major criterion for characterizing polyethylene. Using this scheme of classification PE is usually referred to as: low density (LDPE: $\rho \approx .92$ g/cm³), and high density (HDPE: $\rho \approx .95$ g/cm³).

The most commonly used and accepted method for the determination of density is by use of a Density-Gradient Column defined by ASTM D1505

standard (2). A small piece of the sample is placed in a column of liquid that exhibits a known density gradient; after it has sunk to its equilibrium level, the density is obtained by reading its position in the column.

The basic principle is sound, but the technique is quite involved and suffers from numerous drawbacks. First, the column must be prepared from a mixture of different solutions of known densities which are carefully added on top of one another. This is time consuming and very much an art. The column, which is isolated from shock and vibrations in a constant-temperature environment, must then be calibrated using standard glass floats. Since the column has a limited lifetime (2 or 3 weeks), this calibration has to be verified periodically. The material (powder, granules, or pellets) for which the density is to be measured is press-molded into plates (roughly 15 by 10 by 0.2 cm) according to standardized procedures (2). The actual measurement is done on small pieces (typically 0.3 by 0.3 by 0.2 cm) cut out of the plaque. The mere action of cutting causes local compression, and as the pieces are small, their density is affected. The frequent practice is to allow the induced strains to relax by thermal conditioning. This again takes time. The pieces are then wetted and are gently introduced into the liquid where they settle in roughly 20 minutes. When a certain number of measurements have been made, the column must be cleared of the material, which is retrieved with a wire basket. Care must be taken not to upset the gradient.

Here, we propose a new method that is based on the propagation of ultrasound and allows for an accurate, reliable, yet rapid determination of density.

EXPERIMENTAL METHOD

Even though it is not common practice to use ultrasonic techniques for the study of polymers (3), some data are available from the literature and sparse results can be found for the sound velocity and density (4, 5). The case of polyethylene has been the object of closer attention (6 to 9) and the various measurements tend to show that a correlation between sound velocity (v) and density (ρ) exists. However, no systematic study has been done in the range of ultrasonic frequencies (MHz) and the precise nature of this correlation is neither clear nor well-defined (8). On the other hand there is the work of Davidse, *et al.* (7) who used resonance method to measure the propagation velocity of low frequency (5 to 10 KHz) oscillations in bars of PE.

Their results on a great number of samples show that the velocity is proportional to density. The technique they used is analogous to that of internal friction and is somewhat involved: electrodes must be attached to the samples and the calculation of velocity takes into account geometrical factors and *a priori* knowledge of the Poisson ratio for the material.

It is our objective here to verify the existence of a possible correlation between the velocity of sound and the density and to describe the correlation. We shall also demonstrate that for practical purposes the measurement of velocity can be used for an accurate determination of density.

In the present study, we have chosen to use an immersion technique (4, 10) because of the ease with which the measurements can be made and repeated. The principle of the method, in which a single transducer is used as both the emitter and receiver of sound, is illustrated in Fig. 1. A high-frequency (MHz) sound pulse travels with normal incidence to the sample (a plaque of thickness d). There part of its energy is reflected back (E_1) and returns to the transducer where it arrives at time $2t_1$ (t_1 being the time for the sound to travel the water path one way). Part of the energy goes through the sample where it meets the second interface at time $t_1 + \tau$. Again part of the energy is reflected, part is transmitted and so on. This gives rise to the formation of echoes ($E_2, E_3 \dots$) which are observed at times $2t_1 + 2\tau, 2t_2 + 4\tau \dots$. Thus, if v is the compressional or longitudinal velocity of sound in the sample, then

$$\tau = d/v \quad (1)$$

In order to obtain v , one needs to know the value of d with sufficient precision so as to achieve the required accuracy. In principle, this measurement could be made using a micrometer but this would be both annoying and not very accurate. The samples, which are rough from press forming, show surface and thickness irregularities so that the value of d to be considered must be some average taken

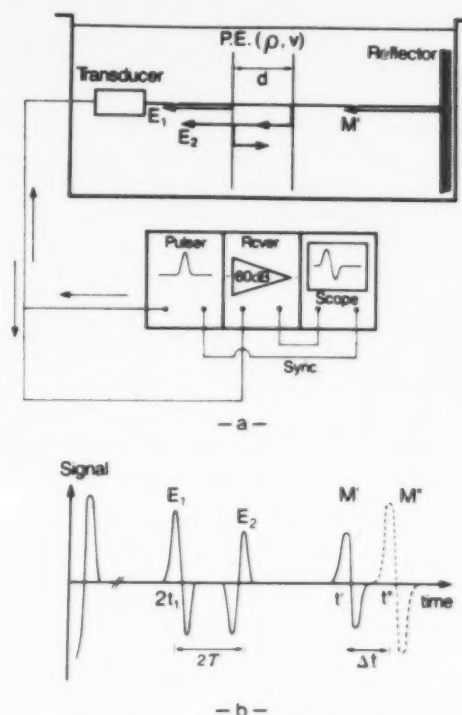


Fig. 1. a) Schematic illustrating the different paths for the sound pulse. b) The corresponding signals observed on the screen of an oscilloscope.

at the location of insonification. The most convenient way to take the thickness into account is through acoustics. Going back to Fig. 1, after part of the energy has traversed the sample, it is transmitted forward in the liquid. This signal can be reflected back to the transducer by means of an acoustic reflector or mirror. If t_2 is the time of flight from the sample to the mirror, the pulse will be observed at time t' :

$$t' = 2t_1 + 2\tau + 2t_2 = 2t_1 + 2d/v + 2t_2 \quad (2)$$

If the sample is now removed, the signal coming from the mirror appears at time t'' :

$$t'' = 2t_1 + 2d/c + 2t_2 \quad (3)$$

where c is the velocity of sound in the liquid. Considering the difference in the times of flight ($\Delta t = t'' - t'$) together with the expression for τ yields:

$$v = c(\Delta t/2\tau + 1) \quad (4)$$

The value of c can be found with great precision so that the velocity (v) is obtained solely from the measurement of time delays, and the method is thus amenable to automation.

EXPERIMENTAL PROCEDURE AND RESULTS

Samples

We shall report the results of sound velocity and density measurements obtained on 35 samples which cover a wide variety of commercial-grade PE. Most of the resins were furnished either by

DuPont Canada or Union Carbide Limited and included LDPE, HDPE, LLDPE, and UHMWPE with densities (11) ranging 0.915 to 0.965 g/cm³. The actual samples used in the measurements are the same form of press-molded plaques (approximately 80 by 50 by 1.9 mm) that are normally prepared for density assessment. In most cases the plaques were made by the resin manufacturer who also indicated the density he had obtained and were used "as is" with no further preparation. However, we repeated the measurement of density with our own density-gradient column in the standard manner. In this way, we were able to define the standard deviation for values of density obtained in different columns. We found $(\delta\rho)_{\text{col.}} = \pm 0.0006 \text{ g/cm}^3$ a value which accounts for all sources of uncertainty and gives a good idea of the reproducibility for this technique.

Ultrasonic technique

The ultrasonic setup which is immersed in a bath of demineralized water at 23°C was designed to accommodate the PE plaques. The transducer is of the commercially (12) available immersion type. In order for the echoes to be separated in time, the pulses must be short; this calls for a highly damped transducer operating at high frequency. However, the attenuation of sound in PE increases rapidly with frequency (4), and this sets an upper limit. The acoustic reflector located approximately 15 cm from the transducer is a flat piece of glass with an absorbant backing so that no signals (echoes) are issued other than the reflection from the front face. The setup is rather simple and the only requirement is that the sample and reflector have their faces perpendicular to the sound beam. A slight misalignment can be accepted but will cause some loss in signal amplitude and degradation of the shape of the echoes, to the detriment of resolution.

Concerning the electronics, we used a Metrotec pulser (Mod. MP203) capable of delivering short (100 ns), high-voltage (300 volts) pulses with a repetition rate of 50 to 100 Hz to excite the transducer. The echo signals are received by an amplifier (Metrotec Mod. MR101) having a 60-dB gain factor and a 20-MHz band width. The RF signal is then monitored on an oscilloscope (Hewlett Packard Mod. 1743A) which is equipped with a dual-time base that allows time-delay measurements with adequate resolution (3 ns or better).

Measurements and Results

First, the sound velocity in water has to be measured. This is accomplished simply by displacing the reflector by a known distance and noting the arrival time. In this way, we found $c = (1.483 \pm 0.001)10^5 \text{ cm/sec}$ at 23°C, a value which agrees well with what is found in the literature (13).

In Fig. 2, we show the results obtained for the measurement of sound velocity in PE as a function of its density. To a good approximation, the velocity is proportional to density.

The results illustrated in Fig. 2 were obtained using a 3-MHz transducer having a diameter of 1.25

cm (1/2 in.). We looked for a possible frequency effect. Our observations are that within 1 percent, there is no dispersion in the range of 1 to 30 MHz. From a fundamental point of view this requires a more elaborate study. Nevertheless, in our pragmatic approach, we found that a frequency of 3 MHz constitutes a good compromise between time resolution and signal amplitude.

On the other hand, since the velocity measured is actually a value taken over the whole region of insonification, we looked at the effect of changing the acoustic beam diameter. Our observations using transducers of increasingly larger diameters (from 0.2 cm for a focused beam up to 4 cm) show that the scatter diminishes. Increasing the diameter amounts to measuring a value that is averaged over a wider area. In order to appraise the scatter, we have measured the velocity at different locations on the same plaques. The results are illustrated in Fig. 3 for a 1.25-cm (1/2-inch) diameter transducer.

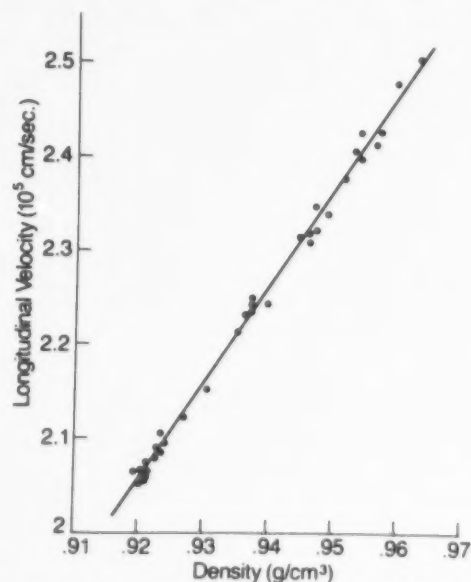


Fig. 2. Longitudinal sound velocity as a function of density in 35 samples of polyethylene (includes LDPE, LLDPE, HDPE, and UHMWPE) of different origins.

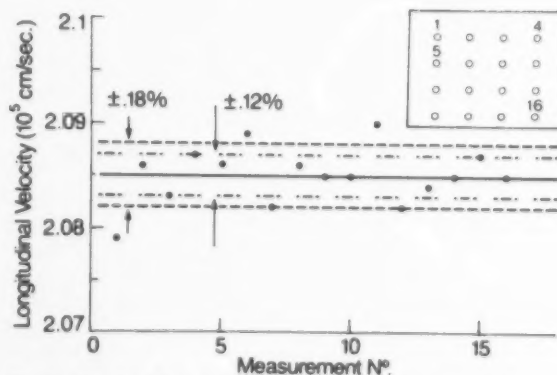


Fig. 3. Standard deviation of velocity as estimated (0.12 percent) and observed (0.18 percent) from sampling at 16 different locations on the same plaque.

The standard deviation is found to be $(\delta v/v)_{\text{exp}} = \pm 0.0018$. However, if we repeat the measurement several times at the same location on the plaque the standard deviation is $(\delta v/v)_{\text{repeat}} = \pm 0.0010$. This tends to show that the scatter partly has its origin in nonhomogeneities found across the plaque.

In turn, we can estimate the theoretical experimental uncertainty by considering the relation from which the velocity is calculated and the various instrumental errors. We obtain a value of $(\delta v/v)_{\text{theo}} = \pm 0.0012$ which is to be compared with $(\delta v/v)_{\text{repeat}}$. Actually such a degree of accuracy corresponds to an upper limit for velocity measurements and is made possible by the fact that the thickness is taken into account acoustically.

These three error factors: $(\delta v/v)_{\text{exper.}}$, $(\delta v/v)_{\text{repeat}}$, and $(\delta v/v)_{\text{theo}}$, are altogether consistent with one another and of comparable values. From this we can conclude that in practice, at 3 MHz, a transducer having a beam width of the order of 1.25 cm (1/2 in) will integrate and average out the inhomogeneities at a representative and meaningful level.

As a last source of uncertainty we can include the effect of temperature fluctuations. Our setup was installed in a room where the temperature was fairly well controlled with fluctuations in the order of $\delta t = \pm 1^\circ\text{C}/\text{day}$. Thus, given the temperature dependence (13) of sound velocity in water $\delta c = 0.002 \times 10^5 \text{ cm/sec}^\circ\text{C}$, we estimate $(\delta v/v)_{\text{temp}} = \pm 0.0013$. This added contribution will manifest itself over a long period of time. Thus, the total uncertainty which can be expected will be in the order of $(\delta v/v)_{\text{tot}} = \pm 0.0025$.

Going back to Fig. 2, we performed a regression analysis of the 35 data points. Using a linear model, $v = a\rho + b$, we find as values for the coefficients and their standard error: $a = (10.32 \pm 0.12) \times 10^5 \text{ cm}^4/\text{g sec}$ and $b = -(7.43 \pm 0.12) \times 10^5 \text{ cm/sec}$. The correlation factor is $r = 0.998$, and more meaningfully, the standard error of estimate is $0.0102 \times 10^5 \text{ cm/sec}$, or, expressed in terms of a relative-average value, $(\delta v/v)_{\text{fit}} = \pm 0.0045$. This value is of the same order of magnitude as expected, but even though the difference is small, $(\delta v/v)_{\text{fit}}$ is larger than either $(\delta v/v)_{\text{exper.}}$ or $(\delta v/v)_{\text{tot}}$. This discrepancy may have its origin in the fact that the samples contain small amounts of additives (11). The sound velocity can be looked upon as a measure of the fundamental elastic properties of the material whereas the density-column method measures the apparent density. The presence of additives will not necessarily affect both quantities in the same manner. With this in mind, $(\delta v/v)_{\text{exper.}}$ represents the error inherent to the technique since it was obtained on a material of constant nature while for the practical purpose of characterizing industrial materials the value of $(\delta v/v)_{\text{fit}}$ must be considered as more realistic since it integrates errors from all sources.

From a statistical point of view, the fit can be considered as very good and this leads us to the conclusion that for PE having a density in the range of 0.92 to 0.97 g/cm³, the room-temperature (23°C) sound velocity is proportional to density.

We may now examine the possibility of using the

measurement of sound velocity for the determination of density in PE with a model such as $\rho = Av + B$. Working the regression analysis with ρ as the dependent variable we obtain $A = (0.0965 \pm 0.0012) \times 10^{-5} \text{ g sec/cm}^4$ and $B = (0.7218 \pm 0.0026) \text{ g/cm}^3$. The correlation factor is of course the same as above ($r = 0.998$) and the standard error of estimate becomes 0.00098 g/cm³ yielding the relative-average value $(\delta\rho/\rho) = \pm 0.0010$. As mentioned above this integrates errors from all sources, and yet it compares quite well with what can be expected when using a density-gradient column for which $(\delta\rho/\rho)_{\text{col}} = \pm 0.0007$. Given this result and bearing in mind that the small difference most probably originates in the additive content, we believe that the ultrasonic approach will allow the determination of density in polyethylene with the required accuracy for quality control purposes.

SUMMARY AND CONCLUSION

We have presented a technique which allows measurement of the value of longitudinal sound velocity in standard plaques of polyethylene with good accuracy. The method is simple and inherently takes into account the thickness of the sample thus avoiding any other measurement. Since it is based on the measurement of time delays, it can readily be made automatic.

Our systematic study on a bank containing a representative number of samples of different grades of PE shows that the velocity at 23°C is without ambiguity proportional to density in the range of 0.92 to 0.97 g/cm³.

The particularly good correlation between the velocity and density leads us to suggest that measurement of velocity be used as a method for the determination of density. Such a method presents a number of advantages over the classical density gradient column, including: no preliminary preparation, the setup is portable, suffers little influence from environment, and requires no special upkeep care; the measurement is quick, reliable, repeatable, and it can be automated (14); standard ASTM press-molded samples are used with no other conditioning, the measurement is nondestructive, and the sample can be kept on file. The overall accuracy is good (0.10 percent), comparable to that of the column (0.07 percent).

In our approach we have been pragmatic, having in mind the industrial application of the method. However, the physical origin for the behavior must still be considered. This will be the object of further work, but we here point out the similarity of our problem with that of the linear temperature dependence of velocity which is interpreted in terms of variations of the free volume (9, 10).

ACKNOWLEDGMENT

The author wishes to acknowledge the gracious participation of Dr. P. Kelly (DuPont Canada) and of Mr. C. Boisjoly and I. R. Lambie (Union Carbide, Canada) who provided both the incentives and the samples for this work.

REFERENCES

1. S. Kavesh and J. M. Shultz, *Polym. Eng. Sci.*, **9**, 331 (1969).
2. *Annual Book of ASTM Standards: Plastics—General Test Methods, Nomenclature*.
3. For a review see: B. Hartman, "Methods of Experimental Physics," Ch. 12, Vol. 16, Part C, Academic Press, New York (1980).
4. B. N. Hung and A. Goldstein, *IEEE Trans. Sonics and Ultrasonics*, **SU-30**, 249 (1983).
5. D. L. Folds, *J. Acoust. Soc. Am.*, **52**, 426 (1972).
6. J. Schuyer, *J. Polym. Sci.*, **36**, 475 (1959).
7. P. P. Davidse, H. I. Waterman, and J. B. Westerdijk, *J. Polym. Sci.*, **59**, 389 (1962).
8. A. Levene, W. J. Pullen, and J. Roberts, *J. Polym. Sci.*, **A-3**, 697 (1965).
9. K. Adachi, G. Harrison, J. Lamb, A. M. North, and R. A. Pethrick, *Polymer*, **22**, 1032 (1981).
10. B. Hartman and J. Jarzynski, *J. Acoust. Soc. Am.*, **56**, 1469 (1974).
11. The manufacturers indicated that their product could contain additives (plasticizer, copolymer . . .) in amounts up to 0.5 percent.
12. Ultrat Laboratories, Inc., Penn., USA.
13. G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants," 14th Ed., p. 66, Longman, New York (1978).
14. L. Piché, M. Dufour, D. Roy, in preparation.

PANEL AND GENERAL DISCUSSION

P. C. Juliano: This panel discussion has as its aim to discuss interfaces - interfaces as in the blends we heard about during the technical presentations and the interfaces between the industrial and academic communities. Improvements in understanding of both these interfaces will have impact on the future of the polymer industry.

The first panelist is Dr. Ahmed Alim from Esso Chemical in Sarnia, Ontario. Dr. Alim joined Esso 10 years ago and has been appointed head of the polyethylene technology division. The second member of the panel is Mr. Klaus Kuhnemann who has been employed by DuPont Canada for twenty-two years, principally responsible for fiber and polymer processing. Dr. Warren Baker, who will make the third presentation, is the founding member of the Universal Consulting Group. He has worked for DuPont Canada as well as for LECO Inc. where he was Vice President for R&D.

I am from General Electric Corp., and represent the area of engineering plastics. Currently I manage the Polymer Physics and Engineering Branch in the Chemical Laboratories. I will address the development of engineering plastics blends and outline several areas of the future research which will have a major impact on the science and technology of polymer blends.

A. A. Alim: At Esso Chemical we produce two types of plastics: PVC and as of a year ago, LLDPE by the Unipol, gas-phase process. I would like to give you a perspective from the resin producer in the commodity business of what we see happening in blends and what needs we have for the future. As has been mentioned during the day, blends are very widely used in the plastics industry. About 10 to 15 percent of all plastics usage is in a form of blends of one type or another. If we look at the past few years we find that the rate of growth of single component plastics was about 4 to 6 percent per annum while of blends (as a proportion of plastics usage) the growth rate was about doubled. The question is: what will happen in the future? The answer depends on whom you ask. There seem to be two schools of thought. One group of analysts tends to think that we will see this trend continue into the foreseeable future. However, another group tends to say that this continuation will occur only for a short period and then we shall see some decline or some oscillation in the rate of growth of blends. The rationale behind that is that there are two opposing factors that manage and control the usage of blends.

Blends are promoted by entry of new resins on the market (or even a new form, such as granular LLDPE). People will try to use the new material as it is, but also will explore the potential of blending

for a number of reasons: to reduce the cost, to impart some desirable properties, for drawability or downgaging reasons, etc. No matter what the resin is people will try to improve on it. Another pro-blending factor is development of machinery, especially mixers and compounders. Here, when a new development capable of producing a higher degree of dispersion occurs, people will try to use it in new applications or applications which were not successful because of poor blending. Another pro-factor is a new application; almost universally, when possibility of a new application develops people will try to blend. As an example—vinyl window profile using impact modified PVC.

On the other hand, there are several factors which will slow the growth of blends. First is convenience. Almost everybody who is using plastics will prefer a single component. Patentability is another reason to avoid blends—unknowingly you may infringe on someone's rights.

Both the pro and con factors put emphasis on R&D. In order to move away from blends to a single component that will do the job, one has to understand why the blend works. It is important to recognize that we should not confuse quantity of R&D, although it is of some concern, with the type, the quality of R&D. Nowadays we see two types of R&D. Resin producers and processors are doing some kind of research aimed primarily at segregating what works from what does not. There is less interest in why it works, or what to do to make it work. On the other hand there is the "academic" type of R&D, which perhaps tends to be more remote from day-to-day industrial practice. There is a gap between the fine ideas developed in long-range academic research and applied development used to solve today's problems in the plant.

In my opinion, the R&D effort should be directed toward the two objectives: to understand why by blending we achieve a certain performance, and to develop a single component to replace the blend. From our perspective the second objective is the main one, but in order to achieve it effectively and efficiently one has to understand why certain blends work and others do not. There are several activities in this area, e.g. reactor-operating mode modification, where one can change the degree of branching or the distribution of molecular weights by simply turning knobs on the reactor. Another method is modification of polymer inside the reactor, e.g. by grafting, copolymerization, etc. These are examples of what we, from the industrial perspective, would like to see happen. Some of this is actually taking place.

To summarize, I see a need for placing emphasis on the type of R&D, trying to bridge the gap between the two extremes I mentioned with the

objective of better understanding "why" and "how" we are getting what we are getting through blending. The ultimate goal would be to substitute blends with a single component.

The mere fact that I am here today and that we are discussing these subjects at the Industrial Materials Research Institute of the National Research Council is very encouraging. I would like to thank Dr. Utracki for this opportunity. This is certainly a step in the right direction. I am also very pleased to mention to you that we have a joint program with IMRI, looking at extensional flow behavior of LLDPE blends. It is this kind of joint research that will tend to bridge the gap and eventually lead to a useful product. Thank you for your attention.

K. Kuhnemann: During the past decade we have seen, particularly in the automobile, appliance, rail, and electronics industry, a rapid displacement of ferrous and nonferrous metals by plastics. Significant inroads were also made in the sports and leisure area, mostly to replace wood. Polymeric materials are now being developed for leaf springs, body panels, car bumpers, fuel tanks, and axles. Plastics are also said to be evaluated in such high-temperature applications as piston rings. These products indicate the expanding opportunities for polymer developments by resin producers, converters, and research institutes such as IMRI.

Because the physical performance of thermoplastics depends on a number of factors and is difficult to predict precisely, in contrast to the steel industry which issues material performance tables, the plastics industry can only provide performance guides. This forces the resin producer and converter to establish strong market-oriented development and customer-service groups. Indeed, the resin converter has become a major player in the successful application of new resins. The sophistication of each partner as well as his process know-how, quality control, and willingness to experiment, will continue to play an increasingly important role in future developments. Today it is readily accepted that new plastic designs require "value-in-use" performance tests before being accepted. Such tests are often a joint effort between the designer, resin producer, and molder - a team which often works at the leading edge of technology where success or failure have become a joint responsibility.

New polymeric blends and composites have become a challenge to the plastics scientists. As we gain new knowledge of the behavior of these materials, and how to control and manipulate macromolecular systems, we find new applications.

During the next years we will be looking for plastics with improved "value-in-use" properties, lower cost, and better utilization of our resources. There is room to enhance the magnetic, electric, heat distortion, optical, flammability, and permeability properties of current commercial polymers. Attention must also be given to the microstructure of compounds. We need better bonding mechanisms between incompatible and antagonistic materials as found at the interphase between immis-

cible polymers and in filler/matrix systems. I should like to give a few examples to underline my point:

1. We heard much about polyethylenes and its impact on the packaging industry. A largely untouched area is the reinforcing of polyethylene, an area which is waiting for new binder technology for the filler/matrix interphase.

2. Silane is a well-known coupling agent for mineral fillers in thermoplastics. Unfortunately, silane forms reversible bonds and hydrolysis can adversely affect physical properties. We need a hydrolysis-resistant coupling agent. Titanates have been mentioned in the literature but I have heard little relating the titanate treatment to physical properties.

3. Some engineering resins are offered with notched Izod impact strength of 0.3-1.0 kJ/m, others with a flex modulus above 1 GPa. However, we have been unable to combine these outstanding physical properties into one thermoplastic resin because the underlying mechanisms for high toughness and high stiffness appear to be incompatible.

4. Parts molded from glass-reinforced resins do not take full advantage of the potential high strength-to-weight ratio available to the designer. Several excellent papers issued on the subject of fiber orientation versus strength of material teach the different failure mechanisms as the glass fiber orients itself away from the load-bearing axis. The fracture strength of a glass fiber embedded in a thermoplastic matrix is reduced by a factor of ten as the fiber orientation changes from axial to normal to the applied stress. Better utilization of resin could be achieved if we learn how to control the orientation in reinforced resins.

5. Glass-filled thermoplastics and associated silane couplings are the technologies quite well established. We understand the mechanisms responsible for the critical fiber length and its dependence on the surface applied sizing. However, we depend largely on the fiber producer's application technology which often is a simple kissing roll arrangement. To get maximum fiber performance, glass fiber requires 100 percent monolayer wetting. It has been shown that this is seldom achieved.

6. Referring again to the critical fiber length, which in turn is a function of the size type and application process, it would be beneficial if glass could be supplied to give preferential breakage at the critical fiber length.

7. Some automotive applications require good paintability and metal-like finishes; there are some problems achieving this with semicrystalline and filled polymers. A better understanding of the adhesion mechanism to filled polymers is required.

8. The last item I should like to mention is bulk-blending technology for the injection molding. The molder attempting bulk blending has three strikes against him: there is no compact hardware to allow gravimetric feeding; he must use volumetric blending, i.e. the process is subject to bulk-density changes; he lacks the proper hardware to do a good blending job even if he could ratio correctly; the general-purpose screws supplied with molding machines need to be designed to give better melt

mixing. Better hardware for the molder would reduce cost to the compounder and permit the molder to participate in resin developments available through bulk blending.

W. E. Baker: I will be a devil's advocate and take it on myself to represent the 1500 or so plastics processors in Canada. Basically, when I look into the future of the polymer blends, I worry that there are some impediments for polymer blends to achieve the full usefulness and opportunity they should. I see these opportunities in two areas: high-performance engineering applications with a high technical content, better handled by major plastics companies, and less sophisticated commodity applications, possibly of the type I spoke of earlier during the meeting. Here are the opportunities for small and medium size processors, to effectively use polymer blends, to improve their product in meaningful ways. The commodity resin producer generally has difficulties in servicing this market. There are a very large and very diverse number of opportunities which are hard for DuPont, Esso, or other major producers to approach. The second difficulty is that blends involve more than one polymer manufactured by a given commodity resin producer. Frequently this leads to a bias, which does not generate optimum polymer blend but rather exploits some market-related opportunities.

When we consider the less sophisticated commodity applications we must realize that the processor is closest to the end market; he deals directly with the end-user, he is the one who has to collect the bills, he is the one who appreciates the commercial problems. Generally he understands the market better than the large chemical company, he grabs the opportunity and services the market in a direct and efficient way. An example is window gasketing, where relatively small compounders and processors developed the blend and serviced the market.

These people need a good polymer blend technology. Unfortunately the processing and compounding industries are not adequately staffed in that regard. They tend to be entrepreneurial types of organizations with little long-term planning. Their market is highly competitive with notoriously low profit margin. Processors rarely have any technical staff and if they do, the staff tend to be mechanical engineering or equipment oriented. The processors do not lean toward the material science side of the business. In addition, it should be said that many processors harbor a mistrust toward the material scientists. This is so because of the differing background, differing terminology, or even operating styles. These are the two solitudes referred to in this month's editorial in *Canadian Plastics* magazine. I would like to make a plea that we try to bridge this gap, recognizing that the problem rests with both parties—the material scientist residing in academia, in a big chemical company or in a governmental laboratory and also with the entrepreneur with all his phobias and attitudes. I believe that here we can do something to help.

There are few ways to do that. First of all, the Canadian Plastics Institute of the Society of Plastics Industry may possibly be an avenue for bridging this. CPI is jointly founded by the industry and government. The Institute attempts to bring technology to the processing industry. I believe that there is a proposal that they position one or two individuals here in this Institute and do some work geared toward the processors' requirements. If this comes to fruition and is managed well that will be a positive development.

I think that there should be more room for joint projects between one or several processor companies and the Industrial Material Research Institute. I have been involved in one such project which was reasonably successful. It was appreciated by the processing segment involved in it.

Another suggestion involves development of better communication with the processing industry. One opportunity that comes to mind is via the Society of Plastics Industry. The SPI has ten different divisions of which seven directly relate to specific plastics-processing segments; e.g. blown film industry, bottle blowing industry, single-use disposable product industry. They have active industrial associations. Many of them have eight to ten meetings a year. Several have newsletters within each group. It would not be that difficult for IMRI, or even university researchers who are interested in these areas, to present themselves to the processor groups, either by presentations, by inserts in the newsletter, etc.

In summary, for polymer blends in the nonengineering area to flourish the material scientists have to bring their contribution to the processor segment more effectively than has been done up to now.

P. C. Juliano: I would like to provide some observations from the material-supplier point of view, based on my association with the industry for over fifteen years. What I am going to present are a few examples of work that has been done within the General Electric Company with engineering plastics. The examples point out how product deficiencies can be overcome using blend technology. The solutions to the problems provided a thorough understanding of the underlying science. This understanding then became the basis of guiding the design of new plastic blends which served much broader markets.

Let me begin with a short history of engineering plastics. In the late 1950's scientists at GE and Bayer invented polycarbonate. That material turned out to be one of the premier engineering thermoplastics. It was transparent and had excellent impact resistance, a notched Izod impact of >16 ft-lb per inch of notch. For many years that material was sold unmodified.

Later, Allen Hay of General Electric discovered the oxidative coupling of 2,6-dimethyl phenol which led to poly(2,6-dimethyl-1,4-phenylene oxide). This material, too, was a transparent engineering thermoplastic. Unmodified, it had a major product deficiency. When injection molded it sponta-

neously stress cracked. The solution to that problem was based on a scientific observation in the laboratory. Several researchers found that polystyrene was miscible with poly(2,6-dimethyl-1,4-phenylene oxide). That scientific observation was translated to a product when it was found that a rubber-modified polystyrene could be blended with poly(2,6-dimethyl-1,4-phenylene oxide) to provide a material with extremely useful properties. As a family of products, they fit very nicely, at that time, in the rather large gap of properties and performance exhibited by other engineering resins. The miscibility of poly(2,6-dimethyl-1,4-phenylene oxide) with the polystyrene portion of the high-impact polystyrene (one T_g) provided a product family with a broad range of heat-distortion temperatures based on the blend composition. This class of polymer blends is a very good example of the translation of a scientific observation to a technically and commercially successful product.

Coming back to polycarbonate, the material was sold for many years as a transparent, high-impact plastic. However, polycarbonate, in very thick sections and in specimens with sharp notches, had much lower impact strength. This product deficiency led to development of polymer blends based on the addition of low-modulus materials in the range of 3 to 10 percent. As long as the low-modulus material was well-dispersed there was a dramatic improvement in the aforementioned deficiencies. That discovery came before the explanation. After the fact we were able to understand the micromechanics of the ductile blends. In the unmodified materials, plane-strain failure occurred. In the blends, plane-stress conditions were created microscopically resulting in high energy absorption and subsequent high impact strengths. With this understanding of the mechanism of impact modification of ductile matrices, we proceeded to understand the polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) blend system since it provides an example of more brittle matrix. Here we developed criteria on how to impact modify this more brittle polymer matrix based on the inputs from the many experiments by our product-development people. In many cases the explanation came after the fact. Nevertheless general, useful rules have been developed as guidelines on how to impact-modify plastics through blending via multiphase systems which have been translated to entirely new families of engineering plastic products.

The last example from the historical point of view is a translation of the blended polycarbonate into a product line for the automotive industry. This blended polycarbonate has been used in instrument-panel applications since, through proper choice of impact modifier and its level, one could design a product with controlled energy-absorption properties. In that application it is very important that a brittle failure does not occur. On the other hand, the instrument panel cannot be so elastic that a head snaps back upon impact. Through material development and understanding of the system one can design an impact-modified plastic with con-

trolled energy-absorption characteristics for instrument-panel applications based on polymer-blend technology. With that material in the hands of automotive engineers there were more applications discovered, especially for exterior auto-body parts. These blends were not suitable for some of the exterior applications due to their lack of gasoline resistance. This product limitation led to the next phase of the development work where a semicrystalline polymer was added to polycarbonate to yield better solvent resistance. Since low-temperature impact resistance was also required, alternative rubber modifiers were found to improve the ductility of these blends. This new blend system is being used in bumper applications in the US and in Europe.

In summary, the point I want to make is that through blend technology product deficiencies can be overcome and custom-tailored products can be designed to fit market demand. The success of this effort resulted from a good interplay of science, product technology, and market development.

Those are historical examples. I think that if you carefully listened to what was said today through all the technical presentations, there was a lot of new, exciting polymer blends research which will translate to the products of the future.

The interpenetrating networks of thermoplastics and combinations of thermoplastics with thermosets are another way to produce useful blend products through processing. As materials, they pose some problems, i.e. how does one continually and reproducibly control morphology of the products which is produced during the processing. The success of several products in the market testify to the success of this approach. In some of the presentations today you heard of the effect of addition of block polymers to the thermoplastics blends leading, in fact, to a thermoplastic interpenetrating network. This area should receive more attention since it would provide us with an additional degree of flexibility in tailoring the properties of blends.

If you do not want to rely on processing to generate the morphological structures, you can learn a lot from research on HIPS and ABS over the years. The rubber morphology of those products is controlled during the polymerization through control of the polymerization process and/or by the use of block or graft copolymers. If you fix the morphology during synthesis then you will not have to worry about process-dependent morphology and properties if the melt-processing conditions are not too severe. The core-shell structures that were talked about in the past give the opportunity to build-in the response of the rubber modifier and of the thermoplastic shell. In this way one can develop various levels of compatibility between the dispersed phase (core-shell modifier) and the matrix.

We have heard a lot today about compatibility, miscibility, and compatibilization. All authors take liberty with the use of these words to describe the state of the components in the blend. Alf Rudin's 1981 review in the *Journal of Macromolecular Science* presents a concise set of definitions which

should be followed. One does not need true thermodynamic miscibility of the blend components to provide the base for useful blend products. The key to useful blend products is the stability of their structure during and after processing.

We heard about some dilemmas in the area of commodity resins blends where there is not much of proprietary position, and where a customer may use three or four different kinds of materials and make a blend product for himself. This situation makes it difficult to obtain patent protection as mentioned by several of the panel members. This is not the case for the engineering plastic blends. The engineering plastic materials business has been built on proprietary knowledge over the years. To expand the scope of the product offerings based on engineering plastic blends it is going to require more than taking polymers A and B of the shelf and mixing them together. This means that some custom-designed synthesis may be required to make stable, useful blend products. This may be a compatibilizer, or an extruder grafted product, etc., but it will be a unique way of putting the polymer components together which will generate reproducible product behavior. It will also be the route to proprietary, unique products.

I want to say a few words about ionomers. They have very exciting possibilities in the polymer blends area. The literature on ionomers is expanding enormously. As we heard today, ionomers can provide means for an entirely new way of securing blend stability by controlling the interactions of the components. I think that we are at a stage where we can take the ionomers from academics and translate them into useful concepts for making products. Here is a great opportunity for the future development.

There are continuously new polymers, new elastomers, and new combinations of these coming to the market. There were people in the past predicting that there will be no new polymers. There have been quite a few new polymers since. Moreover, in the polyolefins area there are new catalysts leading to new structures. From the materials science point of view their behavior is new and different so these are, in effect, new polymers which require us to reexamine them in blend systems to see if there are new possibilities for new products.

My last comment touches on the growth of blends, *per se*. All of the different talks which we heard today focused on very specific applications for blends. Little niches are built for this plastic and that plastic. It is important to recognize that niche-filling constitutes a large volume for blended plastics. However, in my opinion the largest growth potential for blends is not in filling these little niches but rather in opening the whole new application areas for plastics. Metals' replacement has to be the major objective. We see it in the bumpers for automobiles, in exterior body panels, and in instrument panel housings. These applications will grow rapidly. Blends offer great opportunity and flexibility in the design of materials to achieve these product objectives. It is this kind of meeting where

the materials people, the applications people, and the processing people get together to discuss the scientific, technological, operational interfaces that provide the basis for progress with polymer blends.

L. A. Utracki: To start the general discussion I would like to express my point of view as to how we see the interfaces Drs. Alim and Baker were talking about. In the Institute we have about 40 people working on plastics covering a broad spectrum from characterization to processing. We have very strongly established activities in rheology, static and dynamic test methods and in CAD/CAM. The three major thrusts are toward: blends, composites, and process modeling.

In selecting the project our preference is to accept one which is important, proposed and executed in part by a number of companies, and related to at least one of the three specified areas. We have been active on the interface in the other sense, characterizing and developing a proper method of deposition of coupling agents on the filler, compatibilizing blends, and studying the reaction between this factor and the end properties. In short, IMRI is developing into an internationally recognized center of excellence in the area of multiphase-polymeric systems. IMRI is one of the more successful research institutions. During the past four forming and organizing years we managed to return to the Canadian economy more money than it cost to build, equip, and staff this Institute. There is no doubt in my mind that Canadian plastics manufacturing, big or small, is in a better situation than two or three years ago. With the Canadian Plastics Institute in addition, undoubtedly the situation will further improve. However, nobody can expect that IMRI & CPI will provide guidance, technical know-how, and R&D service to 1500 companies.

Other areas of interface activities are the various meetings, conferences, and symposia we are organizing. Besides the three annual minisymposia on blends (in April), composites (in November), and process modeling (in February), each year we host a three-day course and workshop: "Professional Development Program" (in May) for the plastics industry as well as nonregular courses especially on extrusion, co-organized with SPI/SPE. The whole idea behind this is to bring people together, to let them develop the common language, and learn their problems and their capabilities to solve them. We are very proud to act as a converging point for the industrial and academic activists in the plastics area. We are trying to heal the "gap" as fast as we can and as well as we know how.

The second subject I would like to raise is related to engineering resins in Canada. We heard Peter Juliano's brilliant exposé in the panel. The concise outline of the GE success story in polymer blends stresses a need for a good science/technology relation, the wider applicability of the know-how learned in a specific application and high economic benefits which are associated with the proprietary technology. During the last year or so I have tried to awaken some interest in engineering materials in

Canada, so far without much success. Currently we are co-organizing a SPE Regional Technical Conference for October 16 and 17, 1984 on "High Performance Engineering Materials." I hope that this may help.

A. A. Alim: If we can ever hope for a solution the odds must be placed on the people who have the problem. If the processor has a reason for concern he should let the problem be known and collectively look for solutions. At ESSO, when we started LLDPE operation we found out that there were clearly some problems in processing the neat resin. We organized a conference inviting equipment suppliers and people who manufacture the extruders, dies, and screws. We tabled the concern. We said here is the new product, here are the advantages, but here are the limitations and opportunities. I was really amazed by the rate of progress since that time. I am not claiming that progress was only due to that but certainly this activity helped in speeding up the rate of progress. Since then we began to see new screws, new low-pressure dies, modifications to the point that now it is much less of a concern than it was then. I would encourage this approach to be used on a larger scale.

P. C. Juliano: I would like also to offer a suggestion regarding the organization of conferences, and the role of IMRI. It seems that we discussed the issues at the end of the day. I do not know how many people from the universities are still here. Maybe the most important part of a conference on blends is to have a preconference *i.e.* to bring the people who have issues to formulate their problems beforehand, and use that as a base to set up the presentations. Everybody is talking about compatibility, phase separation, etc., in both scientific and practical terms. However the end-processor has been very far from the science. He needs some help in the translation of the science. He should work to close the gap by trying to formulate and identify scientific issues. Coming from the other side, those who work in materials science or processing should close the gap too, by trying to translate their work in terms that others can understand and use. I think that these conferences are good mechanisms, but maybe could be organized to focus on the issues.

W. E. Baker: Clearly there is a gap. But the processors' segment is very substantially at fault for these problems. There is a tendency not to hire enough engineers and chemists. When one sends mailings about these conferences only the technical persons can respond—the nontechnical will not come. Dr. Utracki mentioned that 50 percent of attendance is from industry. But probably 90 percent of them are from large chemical companies or plastics manufacturers. I would like to see 25 to 50 processor companies represented here. I am not certain how to do that.

K. E. Kuhnemann: Developments in plastic compounds fall into two areas, fundamental and applied

research. Much of our effort is in the latter category where there is a competitive environment and a market pull. We often respond to market needs and opportunities and usually expect to recover our costs for new developments. If that market advantage is for some reason lost, we may abandon the project. I see some difficulty working with IMRI in this environment where, when a need disappears, the company will invoke the sunset clause. Another problem is, of course, that IMRI work usually is public knowledge and key proprietary information would quickly be picked up by competitors. Researchers in industry must develop their own projects once they have been given the market needs. Marketing people are often very precise in what the market wants; they will also never leave you without the final question: "When can I have it for market trials?" Could IMRI work in this environment? One area where I see good cooperation develop between industry and educational institutes is in the sharing of some expensive analytical hardware which requires highly skilled operators. Such an arrangement has worked out well between our company and Queen's University at Kingston.

A. M. Catani: We just started a new project "Analysis of problems in the plastics industry," which will involve technical and developmental work on a short-term basis. Hopefully this will start the ball rolling. We have also been working with SPI/CPI giving courses to small- and medium-sized companies at the level of operators and foremen on extrusion.

A. Low: I am one of the processors here. My main concern is confidentiality. If we disclose to academia some of our proprietary techniques for processing, what protection do we have? We have to be accountable as are GE or ESSO. We have to have protection.

A. A. Alim: You can work with material scientists and still protect your confidentiality. It seems that we are taking two extreme positions. I believe that you can reach a mid-position where you can work together and protect the proprietary side of your business. One of the big benefits of meetings such as this is the exposure to problems experienced by others. In many cases you may be able to generate ideas concerning your problem just by observing how similar ones have been solved, without disclosing any information about your operation at all.

P. C. Juliano: These issues are not easy to resolve. I have been on the advisory board of the Cooperative University of Massachusetts Industrial Research Program (CUMIRP) set up about four years ago. It is partially funded by the National Science Foundation and by the industrial sponsors and was initiated to promote cooperation between the university and industry. The same issues kept coming up regarding proprietary rights during the organizational meetings. In many cases, these issues were resolved by having the University work on the basic

understanding and phenomena-related subjects with the industry helping the university focus on several theme areas, *i.e.* thermosets, surface science, liquid crystalline polymers, etc. In this way chemists, physicists, and engineers on the faculty work on the same set of samples and provide a unified knowledge base. None of these systems are commercial but is the understanding of the principles which counts. I am certain that we had intelligent people sitting in this room listening to the presentations today who can translate the information presented and germinate ideas for their own research. It is not the specific solution to the problem but rather idea generation which is important for the university/industry interface to work properly. Trying to have universality to solve an industrial problem, *i.e.*, coming up with packaged solution is not the best use of academia. The industry has the resources to translate an idea into product. I do not think that a university or IMRI have means to do that, but they can provide understanding so people can solve their problem themselves. As an aside, the example of U. Mass. was interesting because there were 15 companies contributing; they were asked for \$15,000 for the first year. In the many discussions on patent rights people lost sight of the fact that the requested amount translated to less than one half of a technician for a year! From our point of view it was important to get involved in focusing the priorities and programs at the universities and to use the ideas they were generating, not to have them to solve our specific problems.

L. A. Utracki: I would like to clarify a couple of points. The Institute is fully supported by the Federal Government. Whatever we do is the property

of Canadian taxpayers, not of any particular company with which we happen to work on a particular problem. We can, and we do, collaborate with companies in such a way that the most sensitive area is protected. Most of the people employed by the Institute came from industries. We are familiar with the importance of confidentiality in industrial work, of the sensitivities regarding the proprietary rights, competitiveness, and the way the market operates. The Institute was created to help industry, and we want to and do help. However, we also need help from the industry—to guide us and to keep us "on track" of the industrial needs. In fact the most interesting, the most challenging problems most often originate from the demands of technology.

P. C. Juliano: I think that we went as far as we can with this discussion. Now it is up to us to work on closing the gaps we talked about. Perhaps the next polymer blends meeting should start with a panel discussion, including a representative from processing industry. In this way everyone can benefit from the panel discussion, not just the hardcore few who are left at the end of a long ten hour day. Thank you.

L. A. Utracki: I wish to thank you all, the speakers for excellent presentations, the panelists so well-led by Pet Juliano, and all participants, especially the active, vocal ones. Thank you for your criticisms, encouragement, advice, and words of praise. The next symposium on polymer blends will be on April 16th, 1985. Prior to that we shall host a meeting on polymer composites on November 20, 1984. *A la prochaine.*

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1A. TITLE OF PUBLICATION Polymer Engineering and Science		1B. PUBLICATION NO. 																																										
3. FREQUENCY OF ISSUE Monthly except Feb., April June, August, October and December when published semi-monthly		2. DATE OF FILING 9/24/84 3A. NO. OF ISSUES PUBLISHED ANNUALLY 18 3B. ANNUAL SUBSCRIPTION PRICE \$75.00 member \$105.00 for non-member																																										
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11. I certify that the statements made by me above are correct and complete		SIGNATURE AND TITLE OF EDITOR, PUBLISHER, BUSINESS MANAGER, OR OWNER Circulation Manager																																										

PS Form 3526
July 1982

(See instruction on reverse)

Society of Plastics Engineers

Executive Office, 14 Fairfield Drive, Brookfield Center, CT 06805, U.S.A.
(203) 775-0471

Telex No. 643-712

MEMBERSHIP APPLICATION



I am applying for:

- ☐ Membership
☐ Reclassification (no charge)
☐ Reinstatement (initiation fee not required)

NAME: _____
First Middle Last

DATE OF BIRTH: _____
Month Day Year

ADDRESS: _____
Fill in both addresses and check your preferred mailing address.

COMPANY (spell out name): _____

City State (Prov.) Zip

POSITION: _____

HOME _____

City State (Prov.) Zip

Job Function

What is the primary end product manufactured or service performed at your company location?

Please Check your Primary job function (check one only):

- ☐ 01 Production or Manufacturing Engineering
☐ 02 Design or Design Engineering
☐ 03 Purchasing
☐ 04 Sales or Marketing
☐ 05 Research or Development Engineering
☐ 06 General or Corporate Management
☐ 07 Other (Specify): _____

DIVISIONS

My free primary Division choice is _____
(check 1, others below as secondary Divisions (cost \$4 each))

- | | |
|---|--|
| ☐ 21 Color and Appearance | ☐ 30 Blow Molding |
| ☐ 22 Extrusion | ☐ 31 Plastics in Automotive |
| ☐ 23 Injection Molding | ☐ 33 Plastics Analysis |
| ☐ 24 Electrical and Electronic | ☐ 34 Decorating |
| ☐ 25 Thermofforming | ☐ 35 Moldmaking and Mold Design |
| ☐ 26 Engineering Properties and Structure | ☐ 36 Medical Plastics |
| ☐ 27 Vinyl Plastics | ☐ 37 Marketing (in formation) |
| ☐ 28 Thermoset | ☐ 38 Polymer Modifiers & Additives (in formation) |
| ☐ 29 Thermoplastics Materials & Foams (Nonvinyl) | |

Grade

Requirements

Senior Member	Minimum of twelve (12) experience credits and current continuous membership in the Society for a minimum of two (2) years.
Member	Minimum of six (6) experience credits.
Affiliate Member	Less than six (6) experience credits.
Student Member	Regularly enrolled FULL-TIME student in a course of study in plastics.

Check below the membership grade for which you believe details of your experience in plastics qualifies you (see grades above).

- ☐ Student Member ☐ Member
☐ Affiliate Member ☐ Senior Member

Statement of Fees (U.S. FUNDS ONLY)

MEMBERSHIP YEAR: 7/1 thru 6/30

\$10.00 INITIATION FEE MUST BE ATTACHED IN ORDER TO PROCESS YOUR APPLICATION. INITIATION FEE IS SEPARATE FROM ANNUAL DUES.

SENIOR MEMBER, MEMBER, AFFILIATE

Annual Dues: 7/1 to 6/30 \$45.00

If joining after 7/1 \$52.50

If joining after 1/1 \$10.00 (initiation fee only)

STUDENT MEMBER

Annual Dues: whenever joining \$8.00 (no initiation fee)

not prorated

REINSTATED MEMBER

Annual Dues: whenever reinstated \$40.00 (no initiation fee)

not prorated

I wish to join the _____ Section

REFERENCES The Bylaws require the names of three references who are familiar with your work. One of them should be a member of the Society. Assistance in providing member-references will be given on request. Signatures are not necessary.

1. (Member-Sponsor) _____
2. _____
3. _____

STATEMENT OF COLLEGE WORK

Years attended		Institution	Major	Degree	Education Credits
From	To				

RECORD OF QUALIFYING EXPERIENCE IN PLASTICS

DATES				Give your title, name and location of employer. List in chronological order. Describe duties fully and state any important engineering work you have done in each position. If space is not sufficient, use separate sheet.	Time in years (a)	% in plastics (b)	Qualifying experience (a x b)
From	To	Mo.	Yr.				

CREDENTIALS COMMITTEE APPROVAL ONLY Approved Grade

(S) _____	Date _____
(S) _____	Date _____
Office use only: _____	Division _____
ID# _____	Job Class _____
Grade _____	Date Elected _____
Section _____	

SUB-TOTAL

Total education and experience credits. ►

I certify that the statements made in this application are correct. I agree, if elected, to be governed by the Constitution and Bylaws of the Society and to promote the objectives of the Society.

Signature in ink. _____ Date _____



INFORMATION FOR AUTHORS

Submission of original and review articles is encouraged. There is no limit on length. Three copies of the manuscript should be submitted, which should be typed, one side only, double space, with at least a 1-inch margin. Submission will be taken to imply that the paper has not been previously published, that it is not being considered elsewhere for publication, and that if accepted it will not be published elsewhere in the same form, in any language, without the consent of the editor or publisher. Authors must agree to transfer copyright to the publisher when an article is accepted for publication. Unless notified to the contrary by the authors, the publisher assumes that the act of submitting the article signifies the authors' agreement to such copyright transfer to the publisher. The journal carries a voluntary page charge. Each manuscript should include:

A separate title page, headed by a concise, meaningful title (avoid abbreviations) for the paper. This page should provide:

- The name and affiliations of each contributing author at the time the paper was prepared
- Indicate by asterisk any changes of address for each author since article preparation.
- Acknowledgment of any prior oral presentation and original source of the material.

A separate abstract page, consisting of a single paragraph of 100–200 words to include the title and the names and addresses of the authors. Define any abbreviations for substances or methods (such as ABS, SAXS, etc.).

A list of references, on a separate page at the end of the text, numbered in order of text citation. The references are to be abbreviated in the form used in Chemical Abstracts using the names of all authors preceded by initials; see Bibliographic Guide for Editors and Authors, American Chemical Society, Washington, D.C.

- Within the text, the reference citations are typed in parentheses in line with the main copy (no superscripts or subscripts), thus:

According to Young, et al. (1) ...

- In the list of references the general style is as follows:

For periodicals:

1. S. S. Young, J. L. White, E. S. Clark and Y. Oyanagi, *Polym. Eng. Sci.*, **20**, 798 (1980).

The journal name and volume are to be underlined and the year is placed in brackets. The issue number is given only when needed for identification. The article name is eliminated unless the reference is unclear without it.

For books: The title to be spelled out in full.

5. H.-G. Elias, "Macromolecules," Ch. 1, Vol. 2, Plenum Press, New York (1977). (Include the state when the city is not identifiable.)

A list of nomenclature, identifying symbols and abbreviations, commonly desirable at the end of the text. Footnotes are to be avoided.

Equations, numbered and typed in the appropriate place in the text. Where symbols cannot be typed, write them neatly in ink.

Tables, each typed on a separate page, with a heading, and numbered with arabic numerals that correspond to the order in which they are cited in the text. The tables should be inserted in the manuscript after the references and before the figures.

Figures, assembled at the end of the manuscript and preceded by a typed list of captions that explain them. Please also supply a set of original figures or sharp glossy photos thereof, on 8½ × 11 paper or attached to sheets of this size, one sheet for each figure. Each should be identified on the front edge or on the back (photographs) with the name of the first author and the figure number (e.g., Smith, Fig. 1). Originals are to be prepared with high contrast India ink and to bear uniformly stencilled notations. Line drawings and photos should be of a quality suitable for good photographic reproduction and retained legibility upon size reduction to one quarter. Manuscript transmittal letter should indicate if the figures need be returned.

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